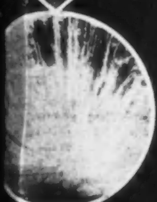
Isotopes at Work

CHEMISTRY



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• A SCIENCE SERVICE PUBLICATION •

Young People in Science

► EACH YEAR it is the privilege of certain members of the editorial staff of Science Service to read the essays written by contestants in the annual Science Talent Search for the Westinghouse Science Scholarships. Each year the readers find that the essays describe more definite projects. This is especially gratifying in the case of the girls, who are often too apt to write in a mood of general benevolence, hoping that Science will make the world a Better Place for Humanity.

To the tough-minded, it might seem doubtful whether that is to be the immediate outcome of certain recent scientific developments. Nevertheless, the attitude of scientific research is still our best guide toward thinking through the political conflicts of our time.

It is, accordingly, a good sign that so many young people, by the time they have reached the 'teen age, are already interested in science, curious enough to lay out definite projects that they want to find out about, and competent to carry through the necessary work. Their joy in this accomplishment, their enthusiasm, their exuberance are always a delight to those attending the Science Talent Institute, when the famous forty get together for five magic days of scientific sightseeing, instruction and discussion in Washington at the end of February.

The profession of chemistry is well represented among this year's winners, and the editors of CHEMISTRY are proud to present some of these essays in this issue. The projects represent fields in which there is plenty of room for investigation, by methods within the reach of young people with home-assembled equipment, and giving results about which the authors can be certain. More power to them!

CHEMISTRY

Vol. 21, No. 7 — Formerly The Chemistry Leaflet — March 1948

Including The Science Leaflet

Published monthly by Science Service, Inc., the institution for the popularization of science. Publication Office: 119 South Frazier St., State College, Pa. Entered as second-class matter at the Post Office, State College, Pa., under Act of Congress of March 3, 1879. Address communications to Editorial and Subscription Office: 1719 N St. N.W., Washington 6, D.C.

25c a Copy; $2.50 a Year. Two-Year Subscription $4; Your Own and a Gift Subscription $4. Quantity Subscriptions, 10 or more copies to same address: $1.70 a Year, $1 for any seven months, 15c each Copy each Month. No charge for Foreign or Canadian Postage.

Editors: WATSON DAVIS and HELEN MILES DAVIS

Consulting Editor: PAULINE BEERY MACK (Editor 1927-1944)

—U. S. Atomic Energy Commission Photo

▸ No RADIATIONS *are given off by the stable isotopes now available for research purposes from Oak Ridge. They can be handled and shipped without risk. The little vial, to be packed inside the larger bottle for shipment, contains Molybdenum 92.*

Atomic Isotopes At Work

▸ EXPLODING ATOMS unknown in nature and unusual varieties of stable elements are at work as tools for the exploration of science's mysteries.

Hardly a field of research is untouched by these by-products of the atomic bomb — medicine, agriculture, industrial chemistry, fundamental biology, and many others.

Because of the importance of isotopes to chemistry as a whole, CHEMISTRY publishes excerpts from the

—U. S. Atomic Energy Commission Pho

➤ THE MASS SPECTROGRAPH *is adjusted by R. L. Caldwell as one of the steps in concentrating separately the two isotopes,* Li^6 *and* Li^7.

latest Atomic Energy Commission report to Congress which tells in broad outline the present status of the isotope program.

Excerpt From AEC Report

Artificial radioactive isotopes were first manufactured in cyclotrons, in minute quantities and at very great expense. Now, as a result of the development of atomic energy, there are more than a hundred kinds available for research work, and in adequate quantities — more than adequate, in fact, in view of the number of technicians qualified to use them. Radioisotopes for off-project distribution are produced in the reactor at Clinton National Laboratory, Oak Ridge.

The stable isotopes are separated from their brother atoms in the great magnetic machines built during the war at Oak Ridge to extract the fissionable U-235 isotope from common uranium. The radioactive isotopes are manufactured by irradiation of materials in nuclear reactors constructed for the production of fissionable plutonium or for research. Thus, isotopes are by-products of the manufacture of the atomic bomb.

But although by-products, isotopes are generally regarded as the most valuable new research tool since the invention of the microscope. If the development of atomic energy had produced nothing else, its cost would undoubtedly have been balanced within a few years by the gains in knowledge that the nation is making with isotopes — gains that are already becoming tangible in medicine, chemistry, industry, and agriculture.

The Commission considers it to be of vital importance to make isotopes available to all qualified users in quantities as large as can be profitably used, in variety as great as can be developed, and at the lowest possible cost.

Nearly 2000 shipments of radioactive isotopes have been made from the Commission's Isotopes Division at Oak Ridge since August, 1946, more than 1600 of them within the past year. Close to 100 different kinds are available. Production and distribution methods have been brought to the point where it is certain that all reasonable future demands can be met. Costs are being reduced rapidly and, for most types, are now well within the range that the average laboratory can afford to pay.

The Commission provides advice on the utilization of radioactive isotopes, together with film badges and other safety equipment, and hopes soon to expand this service to the point where all inexperienced prospective users are instructed in the most productive and safest research techniques.

In September, 1947, the President in a message to the International Cancer Research Congress at St. Louis, announced a program of foreign distribution of isotopes by the Commission. Twenty varieties, particularly those most important for biological and medical research, are now being made available in limited quantities to foreign laboratories and medical research groups, upon prior agreement by the recipient to make six-month reports to the Commission on results obtained and freely permit publication of such results; to use the isotopes only for purposes stated in

—U. S. Atomic Energy Commission Phot

➤ CHEMICAL ANALYSIS *follows the separation process in preparing stable isotopes for distribution to research centers. In the Oak Ridge electromagnetic process plant, J. A. Kinnane and Miss Katy Seeley are working on the Tin isotope,* Sn^{115}.

the original requests; and to permit qualified scientists of all nations to visit their institutions and freely obtain information about the work, in accordance with the best scientific tradition. By the year's end, 20 shipments had been made to foreign users in Argentina, Australia, Denmark, and United Kingdom. To date, as the result of requests received, the Commission has approved future distribution to Belgium, Canada, Cuba, France, Ireland, Italy, the Netherlands, New Zealand, Peru, Sweden, and the Union of South Africa.

Intensive development work in the Oak Ridge electromagnetic separation plant made possible the recent announcement of the availability of more than 100 types of stable (non-radioactive) isotopes for distribution in the United States, and some 200 shipments were made in 1947.

Liaison is maintained with the National Bureau of Standards on radioactivity standards and safety, the U. S. Department of Agriculture and state agricultural experiment stations on agricultural utilization, the National Research Council on cancer research, and the medical agencies of the Armed Forces.

A new Committee on Isotope Distribution was named to advise the Commission's Isotopes Division on the most productive and safest distribution, particularly where therapeutic treatment was planned. Members of this Advisory Committee are: Dr. G. Failla, of the Columbia University Medical School, chairman; Dr. H. A. Barker, plant nutrition, University of California; Dr. Henry Borsook, department of biochemistry, California Institute of Technology; Dr. Robley D. Evans, Massachusetts Institute of Technology; Dr. Hymer L. Friedell, Lakeside Hospital, Western Reserve University, Cleveland; Dr. J. G. Hamilton, University of California; Dr. Joseph W. Kennedy, Washington University, St. Louis; Dr. Robert F. Mehl, Carnegie Institute of Technology; Dr. Paul C. Aebersold, chief, Isotopes Division, AEC, Oak Ridge; Dr. Austin M. Brues, Argonne National Laboratory, Chicago Directed Operations, AEC; Dr. A. H. Holland, Jr., medical adviser, Oak Ridge Directed Operations; Dr. L. N. Nims, acting head of department of biology, Brookhaven National Laboratory, AEC.

Tagged Atoms Help Agriculture

➤ Uncle Sam's tagged atoms range through the chemical alphabet all the way from antimony to zinc, and they can be used in finding new facts about the foundations of agriculture, all the way from how crop plants take up fertilizer out of the soil to how a hen turns crushed oystershells into whole eggshells.

At a conference on the use of radioactive isotopes in agriculture held at the Alabama Polytechnic Institute, Dr. Paul C. Aebersold of the U.S. Atomic Energy Commission, with headquarters at Oak Ridge, Tenn., told of the novel and important wares he has to sell. Among the elements needed in quantity by both plants and animals for their life-processes, only nitrogen and oxygen are unrepresented on the

"tagged" list; such elements as carbon, hydrogen, sulfur, phosphorus and potassium, without which no life can exist, can be supplied to plants and animals in the radioactive forms which can be detected wherever they go by the ticking of a Geiger counter or by exact quantitative analysis.

"Trace" elements, vital though needed in almost imperceptible amounts, are also supplied in "tracer" form, easy to follow through their radioactivity. These include copper, cobalt, nickel, iron, molybdenum, iodine and zinc. The only important trace element that cannot be produced in radioactive tracer form is boron.

The non-radioactive, or stable, forms of many elements are also usable in biological and agricultural research, even though their course through plant or animal bodies is less easily traced than that of their radioactive "opposite numbers." Dr. Aebersold listed 13 of these stable isotopes now available, including nitrogen and oxygen which do not come in radioactive form.

Biology and Medicine Research

Organization of research in biology and medicine by the U. S. Atomic Energy Commission was described by Dr. John Z. Bowers of the Commission's Washington headquarters.

Isotopes are being sold to many universities in this country and several abroad, to be used in their own laboratories. Along with the research elements themselves, qualified scientists of the Commission are available for consultation on problems connected with their use.

For problems beyond the reach of ordinary university or technical school laboratory facilities, several regional research laboratories have been established in cooperation with a large number of educational institutions. To these researches scientists and graduate students can come with their toughest problems. The regional laboratories, working with the universities, will also undertake the training of new research workers in the techniques of atomic-age science.

Safety Techniques Described

Radioactive elements are of course dangerous to handle, and research workers using them will have to become accustomed to certain safety routines. Some of these were described by Dr. G. Williams Morgan of the Atomic Energy Commission, Oak Ridge.

Containers of radioactive materials are kept at more than arm's length with long-handled tongs, and when transported are heavily lead-shielded. Workers constantly carry one or more devices that indicate when they have been exposed to more than the largest tolerable "dose" of radiation and must stay away for a while.

Radioactive dusts are particularly guarded against. Workers in laboratories where this kind of contamination is at all likely to occur change clothes completely before going home at night, to avoid carrying dangerous materials home with them. Since contacts are especially likely to be made with hands and feet, a special checking-machine on which the worker stands for a short time gives him a reading, on four separate dials, of how "hot" his extremities are. Various ingenious adaptations of the Geiger counter are used for probing his

working area, to see if any radioactive material has been inadvertently spilled, creating danger-spots that must be decontaminated.

"Tagging" Traces Phosphates

A revolution in agricultural research is being caused by the use of radioactive "tagging" of elements in fertilizer and other products.

What happens to phosphorus in the soil and after this important fertilizer element has entered the plant has been studied by Dr. S. B. Hendricks of the U. S. Department of Agriculture. He worked at the Department's great experiment station at Beltsville, Md., using compounds of radioactive phosphorus, P^{32}.

Even in soils in which there is no lack of natural phosphorus, plants readily take up added phosphorus applied as fertilizer. Analysis of various parts of crop plants showed that phosphorus is distributed throughout the plant body with remarkable evenness. The only spots favored with higher concentrations are the cotyledons or seed-leaves, which supply stored food to seedlings during the first few days of their lives.

Sulfur, Arsenic Distribution

Sulfur, needed in moderate quantities by all living things, can be taken up by plants either from sulfur compounds in the soil or from sulfur dioxide gas in the air. Dr. M. D. Thomas of the Department of Agriculture, whose research headquarters are at Salt Lake City, followed the course of radioactive sulfur through the plant. He found that its highest concentrations are found in parts of the seed, in the green spongy cell-tissue of the leaves, and in the cambium or growing layer and the phloem or transport-tubes in the stem.

Arsenic, which is something of a problem-element in orchards and fields where it is used year after year as an insecticide, does not get very far into the plants. When radioactive arsenic was supplied to growing plants, practically all of it was stopped in the fine outer roots. Concentration there was from 10 to 100 times greater than that in the remainder of the plant.

Some plants seem to be more tolerant of arsenic than others, the speaker continued. Radishes, for example, took much more of the poisonous element into their storage-roots and leaves than did carrots or beets.

Leaves are poor absorbers of arsenic, further studies showed. When a leaf was dipped into an arsenic compound in solution, the poison remained almost entirely in the zone of contact.

Cobalt in Cow Traced

What do cows do with cobalt? They do not need much of this chemical relative of iron and nickel—one thirty-thousandth of an ounce a day suffices for a half-ton cow—but without that micro-ration they do not stay healthy long. Up to now, the role of cobalt in a cow's bodily economy has remained a physiological riddle, but thanks to the new scientific technique of tracing elements in the body by making them radioactive, the answer has been found.

Cows use cobalt when they make new blood for themselves. Dr. C. L. Comer of the Florida Agricultural Experiment Station has found that only a fraction of a radioactive cobalt compound given to the cow either with her feed or by direct injection into a

vein is retained in the body; the rest is quickly eliminated. Analysis of various parts of the animal's body after slaughter showed that a substantial part of the cobalt was deposited in spleen, red bone marrow, stomach lining and other places where red blood cells are formed. A good deal went to the liver, whence it was secreted into the bile.

Medical Uses of Isotopes

Radioactive isotopes of various elements are used in medicine. Dr. D. Harold Copp of the University of California suggested that some of the uses of these elements in human medicine might be adapted to the needs of the veterinary practitioner.

Tendency of iodine to concentrate in the thyroid gland was used to advantage in studying various diseases of that gland, Dr. Copp pointed out. By giving heavy doses of radioactive iodine, it was found possible to destroy over-active thyroid cells and thus correct at least one of the glandular difficulties.

Because phosphorus plays an important part in the fat metabolism of the body, he continued, the radioactive isotope of that element has been used in studies of that body activity. Phosphorus is also an important constituent of the bones, so that in its easily traced radioactive form it is useful also in bone growth and research.

Carbon monoxide poisoning has been studied by the use of the short-lived radioisotope of carbon, C^{11}. Also, because radioactive isotopes of the rare atmospheric gases argon, krypton and xenon are available it has been possible to push further the study of "bends," the painful malady of divers and aviators caused by bubble formation in the blood.

Dr. Howard B. Skipper of the Southern Research Institute at Birmingham, Ala., told of the use of radioactive carbon, C^{14}, incorporated in the compound known as urethan which is now being used in the treatment of leukemia and other cancer-like diseases. Of special value were data obtained on the chemistry of the drug's breakdown within living tissues.

Antiseptics in Refinery System

➤ GASOLINE and fuel oil output in refineries can be kept at a peak by the use of antiseptics added to the water used in the cooling system. William A. Hall and Roy F. Weston of the Atlantic Refining Company, Philadelphia, explain that the chemicals prevent the formation of slime by water-borne bacteria.

Small amounts of chlorine, phenol, or other germ-killing chemicals in the water keep the equipment almost entirely free from choking slime for as long as four months. Without these chemicals, an accumulation of slime necessitates frequent shut-downs of apparatus for cleaning. The slime also impairs cooling efficiency.

The bacteria themselves comprise only about 25 per cent of the slime of the deposit, the rest consisting of minerals and debris entrapped in it. From studies made it has been shown that it is not only possible to keep the cooling unit in an essentially clean condition by use of the antiseptics, but that once the unit had been fouled, water treatment gradually cleaned it.

Cosmic Ray Showers Born Of Sun Energy Near Earth?

Artificial Mesotrons Created

➤ Creation of mesotrons (or mesons) is the giant Berkeley cyclotron on Feb. 21 is rated as the most significant event in atom study since the discovery of the fission of uranium that led to the atomic bomb.

Found previously as a secondary cosmic ray particle, this particle intermediate between electron and proton was manufactured by hurling 380,000,000 electron-volt alpha particles (helium hearts) against carbon, beryllium or other targets.

The experiments were done by Dr. Eugene Gardner, research physicist in the University of California Radiation Laboratory, and Dr. C. M. G. Lattes, a Brazilian scientist from the University of Sao Paulo, on a Rockefeller Foundation fellowship.

Dr. Lattes worked previously with a group of scientists at the University of Bristol (England) studying cosmic rays with photographic emulsions.

The existence of the meson was first suggested in the 1930's by the Japanese scientist, Dr. Hideki Yukawa to explain a gap in the atomic theory of that day. Such a particle with mass 200 times the electron mass was later found in cloud chamber experiments by Dr. Carl D. Anderson of the California Institute of Technology. He called it the mesotron, and this name has been used interchangeably with meson.

Mesons created in the big cyclotron have a mass of 313. One plate exposed for 30 seconds yielded 100 times as many mesons per plate as were obtained from cosmic rays on a mountain top in 45 days.

Mesons recorded in the photographic emulsion have characteristic wavy tracks, about half of them ending in "stars" due to detonated nuclei.

Just as the neutron, unknown a few years earlier, was the key that unlocked atomic energy, so the mesotron may explain the mystery of the forces that hold the atom together. Already three weights of mesotrons are known and physicists expect that other varieties will be found during their searches on this new atomic frontier.

To duplicate under controlled conditions what the harder cosmic rays can do, hope was expressed by Dr. Leland J. Haworth, assistant director of Brookhaven National Laboratory on Long Island, N.Y., that there would be constructed two giant accelerators operating at billions instead of mere millions of electron volts. The top energy of these machines would be ten billion electron volts. Plans for a similar machine on the West Coast at Berkeley were announced earlier.

Showers Near Earth Is Theory

Showers of cosmic rays may be born close to the earth where radiations from the sun strike local clouds of cosmic dust, the stuff from which meteors are made. This theory which makes cosmic rays a local phenome-

non, has been presented by Dr. Donald H. Menzel of Harvard College Observatory.

Cosmic-ray showers are created out of local clouds of ions found in space within a few million miles of the earth, according to the new theory. Long-wave radiations from the sun give these ions energies as great as 100,000,000,000 volts. The neutron component of the cosmic rays comes from the splitting of heavier atoms into neutron-proton constituents as cosmic rays encounter the earth's atmosphere.

Cosmic rays come in groups rather than one or two at a time. The researches by Dr. Menzel and Winfield W. Salisbury offer a working theory that may also aid study of the ionosphere, radio-echoing layer of atmosphere surrounding the earth.

Fluctuations of the sun, associated with the gustiness and turbulence of the solar atmosphere, cause radio noises of very low frequencies that are sometimes heard here on earth. Because of their long wavelengths, these radiations can escape from the sun, especially in regions where magnetic fields reduce the conductivity. The energy is also known to penetrate the ionosphere.

The radio waves responsible for the cosmic rays also produce other effects. They cause appreciable heating of the solar atmosphere, and lead to the million-degree temperature of the solar corona. The emission exerts a cooling action on sunspots. The light of the night sky and aurora borealis are electrodeless discharges in the electric field of the radiation. Other effects include certain types of ionospheric disturbances and the existence of a potential gradient in the earth's atmosphere.

Italy Offers Peak Laboratory

The high-altitude laboratory at Pianrosa, near Cervinia in the Italian province of Aosta, may become an international center for European scientists studying cosmic rays. This was suggested at the conference on cosmic rays held in Cracow, Poland, under the auspices of UNESCO.

This laboratory, which was prefabricated and transported to a site nearly two miles high, includes both a large laboratory, 20 by 30 feet, and living accommodations for four persons. A cable railway connects it with a guest house 3,000 feet below. Food and materials are procured at the lower station and eight more persons can stay at the guest house. The unique laboratory is open all the year.

Director of the cosmic ray center is a young Italian scientist, Gilberto Bernardini, who is a visiting professor at Columbia University in New York during the first six months of 1948. During his absence, Prof. E. Amaldi, director of the Nuclear Physics Center in Rome, and Dr. Ettore Pancini are in charge of the high-altitude cosmic ray research.

Several different attacks on the problems of the meson are being followed by Dr. Bernardini's group. They are using counters to study the absorption of mesons near their extreme range; the spectrum of mesons is being analyzed with iron cores; the production of mesons in different materials is being tested; and Wilson chambers are employed in absorption experiments.

Elements Heavier Than Curium Predicted by Dr. Seaborg

Synthesis of 97 and 98 Difficult

➤ THE SYNTHETIC manufacture and identification of chemical elements heavier than curium, number 96, tops in atomic number and weight, will be possible.

The major difficulty in making new undiscovered elements 97 and 98 will be finding the necessary starting materials. Dr. Glenn T. Seaborg of the University of California in the Sigma Xi lecture before the American Association for the Advancement of Science predicted that the most stable and the longest-lived varieties or isotopes of elements 97 and 98 will have masses as high as 247 and 248 and higher.

Curium's heaviest isotope is only 242 and from it upward is quite a jump. However, Dr. Seaborg has some good guesses about the chemical properties of such new elements, and he will use this information in attempting to create the new elements in the future.

Co-discoverer of atomic bomb element, plutonium, 94, as well as americium, 95, and curium, 96, Dr. Seaborg explained that of the 96 known elements, 94 have been isolated in quantities sufficiently large to see and weigh them. Astatine 85 and francium 87 may never be separated out in such quantities and in Dr. Seaborg's opinion may remain unique in being the rarest of chemical elements.

Eight chemical elements, four of them beyond uranium 92, and four filling gaps in the periodic table, at 43, 61, 85 and 87, have been discovered within the past ten years.

The metals gold, silver, copper, iron, lead, tin, mercury and also possibly zinc, as well as the non-metals, sulfur and carbon, were all known and written about some 2,000 years ago. A number of these were known 5,000 years ago and some probably were recognized and used in prehistoric times. The alchemists identified the substances arsenic, antimony and bismuth during the period from the twelfth through the sixteenth centuries. Platinum was probably the "white gold" of that period.

The first individual identified as a chemical element discoverer was a German merchant, Hennig Brandt, who first brought to light the element phosphorus in 1669. A dozen elements were discovered in the eighteenth century, while most of the remaining elements, about 60 in all, were discovered in the nineteenth century.

During the war, "nickels" were made of an alloy of copper, silver and manganese; nickel is now being used again.

Cyclopentenylamines have been identified as a new group of insecticides.

For the Home Lab

The Canizarro Reaction

by Burton L. Hawk

➤ When certain aldehydes, such as benzaldehyde and formaldehyde, are treated with alkali, a simultaneous oxidation-reduction occurs. In other words, one molecule of the aldehyde oxidizes another molecule at the expense of being reduced itself. This process is known as the *Canizarro* reaction, named after its discoverer, Stanislao Canizarro, (1853). As a result of this reaction, we can obtain the corresponding acid and alcohol of the aldehyde. For example:

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + KOH \rightarrow \underset{\text{Potassium Benzoate}}{C_6H_5COOK} + \underset{\text{Benzyl Alcohol}}{C_6H_5CH_2OH}$$

We will attempt a demonstration of the above, using benzaldehyde as our starting point.

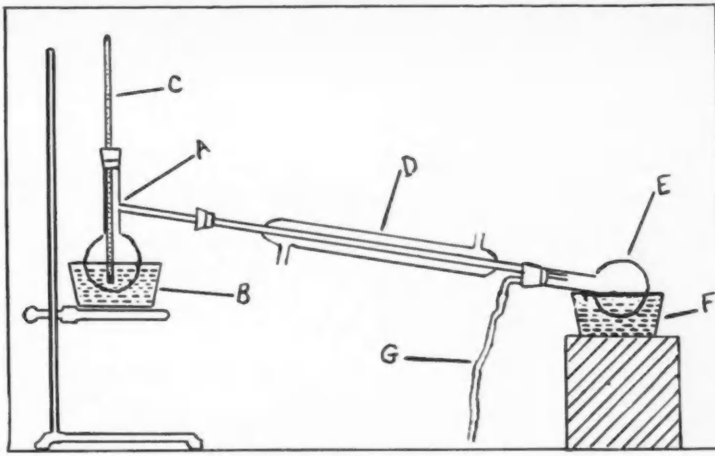
First, it is necessary that the benzaldehyde be freshly distilled. About 7 cc. will be required. It is advisable to add small pieces of clay plate or glass beads when distilling in order to prevent bumping.

Next, a concentrated solution of potassium hydroxide is prepared. Dissolve 6 g. of the compound in 5 cc. of water. After all is dissolved, cool the solution thoroughly and add it to the freshly distilled benzaldehyde in a small flask. Stopper the flask with a cork and shake vigorously. (Do not allow the alkali solution to come in contact with the skin or clothing.) A white milk-like emulsion will be formed. This should be allowed to stand for 12 to 24 hours.

At the end of the designated time, potassium benzoate will separate as a white precipitate. Add just enough water to dissolve it, forming a clear solution. In addition to the potassium benzoate, the solution also contains benzyl alcohol. To obtain the alcohol it will be necessary to extract it with ether, proceeding as follows:

Pour the solution into a separatory funnel and add 5 cc. of ether. Shake thoroughly, and let stand until two definite liquid layers are formed. Drain off the bottom aqueous layer, and pour off the ether layer through the top of the funnel into a test tube and stopper it. Pour the aqueous solution back into the funnel and repeat the process, adding another 5 cc. of ether. Repeat once again, and then combine the three ether extracts. The ether should now be dried. This is accomplished by shaking with *anhydrous* magnesium sulfate. (The anhydrous compound can be obtained from ordinary Epsom salts by heating in a porcelain or glass dish, stirring with a glass rod, until a white powder is formed.) After shaking, allow the ether solution to stand for about 10 minutes (stoppered).

While waiting for the ether, let us turn our attention to the aqueous potassium benzoate solution. In a beaker mix together 10 cc. of hydrochloric acid with 10 cc. of water, and add a small quantity of cracked ice.



Distillation of ether

While stirring, pour the potassium benzoate solution into the iced HCl solution. Benzoic acid will separate. Filter, wash, dissolve in hot water and recrystallize.

In order to obtain the benzyl alcohol from the ether solution, it is necessary to distill. Because of its high inflammability and explosive characteristics, the utmost caution must be exercised whenever ether is distilled. The safest procedure is to set up an apparatus as shown in the accompanying diagram. Distilling flask (A), containing the ether solution, is immersed in boiling water in container (B). Thermometer (C) is inserted in flask extending into liquid. If condenser (D) is not available, a straight piece of glass tubing will suffice. Condensed ether collects in flask (E) which is immersed in ice water (F). Rubber tubing (G) leads any ether which has not condensed below laboratory bench where it cannot come into contact with open flame. Container (B) must be refilled with hot water from time to time. Or, if you desire, a small flame may be placed under the container providing all connections are tight. In any event, keep the liquid in the flask under 70°. The distilled ether can be saved and used again.

After all ether has distilled over, benzyl alcohol will remain in the flask. To purify, distil the alcohol and collect that portion boiling from 200 - 207°. As this experiment was designed primarily to illustrate an important organic reaction, the yield of alcohol will be very small. If a larger quantity is desired, it will be necessary to increase the amount of reagents used proportionately throughout the experiment.

Formaldehyde, when treated with KOH, will yield formic acid and methyl alcohol, but these products are more difficult to separate.

Chemistry in Patents

To obtain complete specifications of any patent, send 25 cents in coin, money order or patent coupon for each copy desired, and order by number. Address the Commissioner of Patents, Washington 25, D. C.

Extracting Oil Shales

➤ An improved method for extracting oil from oil shales, which will have to supply us with part of our liquid fuels and lubricants after our oil wells run dry, is offered by Harry D. Brown of Rifle, Colo., for patent 2,431,677. Instead of "cooking" the oil out by batches in a retort, he runs a continuous process, in which the ground shale is first mixed with a catalyst, then suspended as a pulp in an oil and pumped through heating coils where the extraction is accomplished. The shale oil is separated from the oily vehicle by standard refining processes, and the latter oil reused. The mineral residue is stated to be useful for soil conditioning.

Dust-Free Fuels

➤ Coal is made dust-free by coating with asphalt from a colloidal suspension in water, in the process on which patent 2,431,891 was granted to C. R. Rosencranse of Pittsburg, Kans. All grades of coal, from anthracite through bituminous to lignite, can be thus protected, the inventor states.

Alloys by Electrolysis

➤ Alloys of magnesium with lead, tin, zinc or bismuth are prepared by an electrolytic method on which L. A. Yerkes of Boulder City, Nev., has obtained patent 2,431,723. A bath of fused magnesium oxide contains a small quantity of a boron compound as a solubility promoter; the cathode consists of the metal to be alloyed, in a molten state.

Nicotine Insect Killer

➤ Finely-ground tobacco so strong in nicotine that not even the most confirmed snuff addict would ever dip or chew it — not more than once, anyway — has just been patented as a possibly profitable commodity. Intended for poisoning insects, it has had its natural nicotine content stepped up to 10% by the addition of straight nicotine sulfate. The pulverized leaf and stem tissue serves as an efficient and low-cost carrier, in place of the mineral dusts hitherto employed. The inventor of this new natural insecticide, Robert B. Arnold of Richmond, Va., has assigned rights in his patent, No. 2,431,672, to the Tobacco By-Products and Chemical Corporation.

Supersonic Inspector

➤ Supersonic vibrations in a fluid are used as a means of inspecting solid bodies of any kind, in the invention on which Benson Carlin of New York received patent 2,431,862. Changes in the wave pattern picked up by receivers tell of flaws or defective shapes in the articles being tested.

Carbon-Molybdenum Weld

➤ A METHOD for welding carbon to molybdenum, desirable in making certain types of tools and machine parts, is the subject of patent 2,431,-975, assigned to the Atomic Energy Commission by two California inventors, Hubert P. Yockey of Oakland and James M. Nuding of Berkeley. The work is done in an atomic hydrogen flame.

New Anti-Glare Surface

➤ A NEW TYPE of glare-reducing surface for lenses and other optical parts is covered by patent 2,432,484, assigned by Harold R. Moulton of Southbridge, Mass., to the American Optical Company. To form it, submicroscopic particles of the transparent fluoride of calcium, magnesium or other light metal are mixed into a thin colloidal suspension in an alcoholic solution of a plastic. This is flowed upon the lens to be coated while it is being spun rapidly, thus insuring fairly uniform distribution. The surface, when hardened, is just irregular enough to disperse incident rays that do not pass through it, instead of reflecting them all in the same direction, producing a glare.

Rare Earth Oxides

➤ A NEW INSULATING material, in which oxides of the rare-earth elements lanthanum, neodymium and praseodymium are mixed with titanium dioxide, is among the few patents granted, on application made before the war to citizens of Axis countries. When issued, such patents are of course taken over by the office of the Attorney General. The inventor of this process (No. 2,432,250) is Werner Rath of Bad Klosterlausnitz, Germany, who claims for his material an unusually high dielectric constant.

Fluorinated Benzene

➤ WHAT MIGHT BE called a super-freon is the subject of patent 2,431,-969, assigned by its inventor, Dr. William S. Struve of Carneys Point, N.J., to the Atomic Energy Commission. Chemically, it is a benzene ring to which nine atoms of fluorine and one of chlorine are attached; its name is fluorinated perchlorohexatriene. It is a liquid that boils at 75 degrees Centigrade, hence should be a good refrigerant. It is also useful as an industrial solvent.

Scratchproof Coats

➤ GLASS LENSES of field glasses, telescopes, range-finders and other optical instruments can now be made scratch-proof, under an armor of a transparent substance harder than steel. A process for vaporizing quartz and depositing it on glass surfaces has been developed by James C. Ogle, Jr., and Arthur R. Weinrich of Brackenridge, Pa., who received U. S. patent 2,432,538 on their invention.

Both melting and evaporation points of quartz are very high, but evaporation is readily accomplished, the inventors state, by coiling resistance wires of zinc, titanium or beryllium around the quartz rods or pieces and passing a current through them. This causes local melting, and the fused quartz is immediately vaporized. The vapor, coming into contact with the cool surface of the glass lens or metal mirror to be protected, "freezes" like water-mist hardening to glaze ice on a winter street. The entire process is carried out in a vacuum. Patent rights are assigned to

the Libbey-Owens-Ford Glass Company.

Super-Soluble Salt

➤ SALT, proverbially the most soluble stuff there is, sometimes does not dissolve quickly enough to suit the user, as for example in the dairy business. To make a cheaper, highly soluble form of salt, J. Grant-Mackay of Drexel Hill, Pa., first melts it, then sprays the melted mass into a quenching bath of water or brine. This produces fine grains under thermal stress, which go into solution quite readily.

Improved Bentonite

➤ AN EXTRA-LIGHT, fluffy form of the remarkable clay known as Bentonite is prepared by Paul Bechtner of Chicago, by giving this thirsty mineral all the water it can soak up, freezing it solid, and then removing the water by sublimation, the direct conversion of ice into water vapor without melting. This very light, fluffy material is highly absorbent and has a thousand possible industrial and domestic uses. The patent, No. 2,433,193, is assigned to the American Colloid Company.

$MgCO_3$ Recovery

➤ THE CARBONATES of magnesium and calcium are frequently found mixed together, and it may be desirable to separate them in order to use the more valuable magnesium compound. The mixed minerals are ground to a slurry with water and carbon dioxide added to get the magnesium compound into solution. When it re-crystallizes, the crystals that form are large enough to be separated out mechanically. Patent 2,433,297 on this method has been awarded R. A. Schoenlaub of Tiffin, Ohio.

Riboflavin From Whey

➤ RIBOFLAVIN, a valuable vitamin in the B-complex, is obtained by fermenting the dairy waste-product, whey, with a bacterial species known as Colstridium acetobutylicum by a three-man research team consisting of N. E. Rodgers, H. L. Pollard and R. E. Meade, all of Appleton, Wis. Rights in their patent, No. 2,433,064, are assigned to the Western Condensing Company.

News About Plastics

➤ A COMPRESSED-AIR gun that will blow out multiple filaments of sticky plastic to form over any desired object coatings that will subsequently harden and "set" is the invention on which patent 2,433,000 was granted to Fred W. Manning of Palo Alto, Calif.

Probably the first really new thing that has happened to paint-brushes in centuries is the use of what might be called "spaghetti" bristles, in the invention on which patent 2,433,325 was issued to Charles E. Slaughter of New Canaan, Conn. The bristles are made of plastic, extruded hollow. Such bristles will take up paint not only by capillary action between themselves and other bristles, as all paint-brushes do; they also pick up paint in their hollow centers.

On the Back Cover

➤ STOPPED *by the treated half of the filter, carbon black streams through the untreated side in a demonstration of the new respirator material developed by the American Optical Co.*

Smoke Abatement Saves Fuel, Promotes Community Health

Fighting the Smoke Menace

A BELCHING CHIMNEY is always a sign of waste. It is a preventable waste. Equally important, the smoke and the gases in it pollute the air and are a definite health menace. Even clean smoke is harmful in the lungs. More harmful perhaps are the sulfur gases, carbon monoxide and other vapors usually found in the smoke from chimneys. The ordinary housewife thinks of the smoke nuisance usually in terms of the extra housework it causes. But injured lungs and poisoned bodies are more important than the cleaning of sooty furniture or washing soot-soiled clothes.

A single house-owner with a smoky chimney does not add much murky smog and poisonous gas to the air. But coupled with thousands of others it adds up. It may even more than equal the smoke from all the factory furnaces and the locomotives in an industrial city. The householder should be the first to start the program of smoke abatement.

With the ordinary home furnace, excessive smoke is due to poor methods of firing. Bituminous coal experts have recently suggested several ways to save coal and prevent smoke by more complete combustion. One simple scheme for the shovel-fed bituminous furnace is to pile the fresh coal in a sloping heap on one side of the firebox, or in a conical heap in the center. The bright fire at the foot of the slope insures complete combustion and the coal rolls into the burning area as needed.

Many cities in the United States have gone far forward in smoke abatement. They are no longer dirty towns. Even airplanes no longer dodge them; smoke over a city or an airport is a definite aircraft hazard. These city campaigns for householders urged the use of proper coal and proper firing. Their campaigns for factories urged or required the use of smoke consumers and other devices to catch the smoke and the harmful gases. Science has long ago found successful means of smoke abatement. It rests with individual cities to put them into operation.

Among the new methods is an English war-time development. It was perfected to stop vessels on the ocean from giving out tell-tale smoke, visible to enemy eyes. The principle involved the use of a stream of air driven into the combustion chamber over the coal. There the air mixes with the gases and vapors formed by the heat of the coal and causes complete combustion. The stream of air is used only when needed, particularly when fresh coal is thrown on the fire. The device, suitable for factory uses, is relatively inexpensive. It saves 5% of the fuel, the British claim.

Steam-air jets have been recently found effective in preventing heavy smoke from coal-burning locomotives. Their effectiveness has been known

—American Optical Co. photo

➤ FOR PROTECTION *against dust, a new respirator, with a felt pad chemically treated to hold back forty times as much dust as the untreated fibers, was tried out on this subject, with obvious results.*

—Association of American Railroads phot

➤ Outbound from Chicago, *five merchandise trains carry needed supplies but add their bit to the city's smoke pall. Railroads are developing equipment to make coal combustion in locomotives more efficient.*

for years but it is only in the past few that satisfactory equipment for the proper installations has been developed. The equipment is the work of Battelle Memorial Institute, Columbus, Ohio. Many locomotives on the Louisville and Nashville railroad are now daily giving testimony of the effectiveness of steam-air jet method of smoke abatement. With adaptations, it can be used with stationary furnaces.

The abatement of smoke from home and factory chimneys begins with education. When coal users understand that visible smoke is largely unburned particles of combustible matter, and that the escape of unconsumed fuel into the air means bigger fuel bills they will take steps to prevent the waste.

Education means also arousing public opinion. It was an aroused public demand that stopped the smoke nuisance in American cities once noted for their dirt but now clean. Housewives, tired of cleaning sooty walls, furniture and clothes, helped awaken

the popular demand. Home-owners, whose pocketbooks were pinched from frequent repainting, also aided.

Visible smoke is soot. Soot is just a mixture of fine particles of unburned carbon, tar and ash. Sulfur and other compounds are sometimes included. It is the tar in the spot that makes it cling to sufaces and clothing. Carbon particles alone, collected on the outside of a building, would wash off with the rain, but rain has little cleaning effect on the tarry mixture.

Anthracite and coke create little smoke nuisance. Bituminous coal and oil contain so much volatile matter that incomplete combustion results in smoke. The nuisance caused by bituminous coal varies greatly with the types used. Certain American cities have done much in abating the smoke nuisance by forbidding the use of coals which tend to create great volumes of smoke.

The combustion space in many furnaces is too small to permit the complete combustion of fuels with a high percent of volatile matter. Experts can tell what kind of fuel can be burned best in any existing furnace firebox. Manufacturers of the furnaces are usually the experts, but several technical schools of the country have mechanical engineers on their staff whose advice is reliable.

Proper furnaces, proper firing methods and proper fuels are the first steps in eliminating belching smoke from industrial chimneys. Sometimes these are not enough, and mechanical or other means must be employed within the chimneys themselves to prevent smoke escapement from the tops. Filtering, blowing and electrical means have all proved successful.

The filter, placed within the chimney, is a porous material that will not burn, such as steel wool, and it is capable of catching the fine particles in the smoke. One blowing method uses the principle of centrifugal force in a whirling column of air to force the particles to the inside walls of the chimney for later cleaning. The electrical method gives the rising particles in the smoke a static electric charge so that they may be attracted to electric plates on the side walls.

Fan-blade traps, cinder traps, a steam siphon system and washing devices have all been used with more or less success. It all sums up to the fact that there are practical means of smoke abatement. The money outlay necessary is returned in fuel savings.

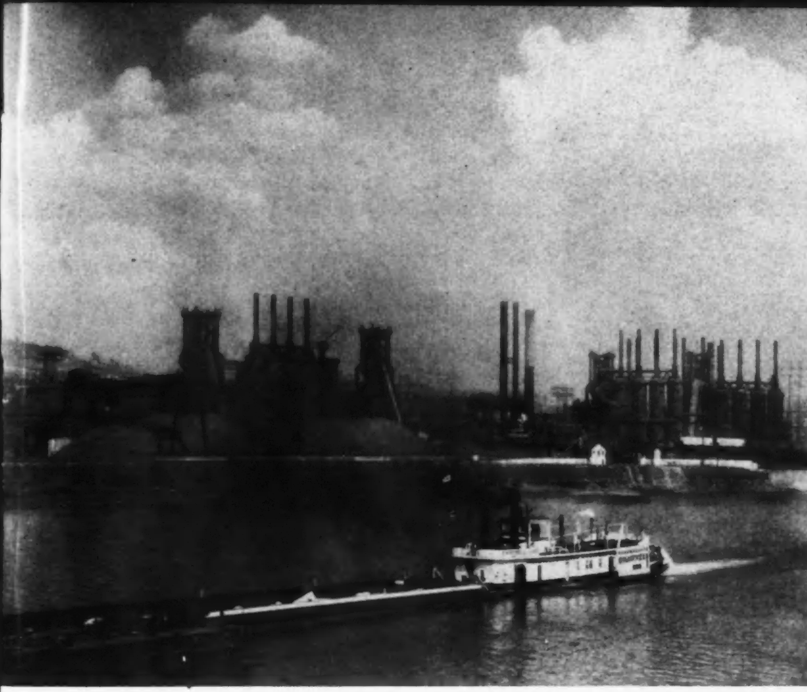
Persons who live and work in an atmosphere badly polluted by smoke run more chance of getting pneumonia, tuberculosis and cancer of the lungs and breathing tract than those living and working in less smoky atmospheres, it appears from a report in the Journal of the American Medical Association.

Death rates from these diseases also are higher in badly smoke-polluted regions.

"Death rates from pneumonia, tuberculosis and respiratory tract cancer provide a clear index of the damage air pollution inflicts on a city's population," the A.M.A. Journal states.

"All three of these diseases show a much higher death and incidence rate in badly polluted areas. This increase takes place mainly in the men who are out in the polluted atmosphere a greater portion of each day.

"The relation between sootfall and



—Carnegie-Illinois Steel Corp. pho

➤ INDUSTRIAL PLANTS *as well as the steamboat contribute to the smog of Pittsburgh, but methods for combatting this health menace are beginning to clear up the air over many American cities.*

respiratory disease death rates is highly significant on a statistical basis and should lead public health and housing authorities to a keener appreciation of the importance of air pollution in the high respiratory disease death rates of slum populations."

Smoky atmospheres may also impair health by depriving inhabitants of the health-giving ultraviolet rays from the sun. The U.S. Weather Bureau reported that in 1945 Chicago received only 56% of possible hours of sunshine. Smoke alone did not cause all this loss, but combined with fog and partial cloudiness it was a factor.

Lack of ultraviolet light means, for most persons, lack of one of the vitamins. This is vitamin D. Babies and children deprived of this vitamin get rickets. To protect them from this serious vitamin deficiency disease, doctors usually prescribe fish liver oil, which contains the vitamin. But few grown persons take fish liver oil, or eat fish livers, and they also need

vitamin D. About the only source of the vitamin for grown-ups, unless they take vitamin pills, is the ultraviolet light of the sun. This light activates a chemical in human skin, turning it into vitamin D.

Anyone who has lived in a smoke-polluted city knows well the uncomfortable, often painful experience of getting a cinder in the eye. Physicians know, as the average layman does not, that foreign bodies in the eye are often the cause of painful ulcers of the cornea. Besides this danger, those who are constantly exposed to the gases and particles of smoke suffer from an irritation which causes a lowering of the natural resistance of the eye to disease, an editorial in the New England Journal of Medicine has pointed out.

In a study of the effect of coal smoke on the lungs, Drs. Lucy Schnurer and Samuel R. Haythorn examined the lungs of rabbits living in an artificial smoky city. The atmosphere of this city was made up of oxygen and flue smoke from an egg stove that burned bituminous coal continuously for a period of 80 days.

Immediately after residence in this atmosphere, the rabbit lungs contained great quantities of carbon phagocytes (scavenger cells that surrounded the carbon particles) and much free carbon. Later the phagocytes began to collect in clumps in the air sacs of the lungs and in various sets of lymph vessels.

The lung changes resembled those of persons living in smoky atmospheres rather than those associated with occupational diseases, the scientists reported to the American Association of Pathologists and Bacteriologists.

The results indicated that carbon in sufficient quantities is capable of producing fibrous changes.

The coal-burning steam locomotive is charged, by the Journal of the American Medical Association, with being "one of the most serious single health menaces in the urban air pollution picture."

The medical journal's statement was in answer to a question from a physician whose local Rotary Club and Civic Association were trying to fight the smoke nuisance from railroad yards in their community.

The locomotive, it was explained, contributes (1) carbon particles, which would be harmless if pure but which have condensed on them varying loads of tars, some of which have been found definitely cancerigenic in animals; (2) fly-ash, which is probably more damaging than carbon soot to the human respiratory tract, especially in setting up chronic irritative states; (3) noxious gases, especially the oxides of sulfur, which form corrosive acids when dissolved in water, and (4) exhaust steam, which itself is not harmful but which is liberated into cold winter air in far greater amounts than the air can hold as invisible water vapor and hence must remain as a steam cloud.

During stable winter weather phases of low air motion there is often formed a stratified ceiling 500 to 800 feet above the ground. Into this pocketed air mass the locomotives exhaust their steam and polluting materials. Natural fog tendencies are thus greatly accentuated, and the suspension and rapid accumulation of all flue products in this surface fog mass leads quickly to "smogs" and a dangerous atmosphere for the people to breathe.

—Photo by Fremont Davis, Science Service Staff Photographe

➤ TOP WINNERS *of the Seventh Science Talent Search, Barbara Wolff, whose project is on factors affecting development of fruit-fly larvae, and Andrew Kende, who is working on improved solvents for Grignard reagents.*

Chemists in the 7th S.T.S.

➤ FROM AMONG the essays written by the forty winners of the Seventh Annual Science Talent Search, the editors of CHEMISTRY have selected the seven that follow as projects of interest to students of that science. No one science is given a preference over any other in judging the entries in the S.T.S. The only question is whether the contestant is already interested in some scientific field and, if so, whether he has "found himself" there sufficiently to begin asking his own questions of nature in the form of an experimental project. The authors of these essays have chosen their projects from chemical problems new and old, because they wanted to know and because they could contribute their individual slants to the general method of attack. They have had fun doing them and they want to go on finding out more. CHEMISTRY is proud to present seven young chemists of tomorrow!

—Westinghouse photo

➤ Andrew Kende *wants to get away from the hazard of explosions when ether vapors mix with air. He carried out a series of experiments in which related substances with higher ignition temperatures were substituted for ether as a solvent for one of the most useful reagents in making organic compounds.*

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Solvent Ethers for Grignard Reagents

by ANDREW STEVEN KENDE, 15.
Evanston Township High School, Evanston, Ill.

➤ THE REACTION of an organic halide with magnesium metal in the presence of ether leads to what is commonly known as a Grignard reagent. This name is the result of the extensive research carried out by V. Grignard, which won for him the 1912 Nobel prize in chemistry.

Although this reagent has, until recently, found few industrial applications, it has for many reasons been the most versatile tool available to the research chemist. It has led to the development of numerous processes which contribute greatly to the comfort of life today.[1]

With the development of the remarkable silicones and other new commercial compounds, such as many of the synthetic sex hormones, the importance of Grignard reagents in industry has assumed new meaning. Heat resistant lubricants,[2] tough, horny resins,[3] and a synthetic rubber that is 90 per cent ash,[4-5] are but a few of the organosilicon polymers prepared commercially by Grignard reactions. Moreover, useful organometallic compounds such as tetraethyl lead[6-9] may be prepared from the corresponding alkyl or aryl Grignards.

In my work with organic silicon polymers, the usefulness and disadvantages of Grignard reactions soon became apparent. The outstanding drawback of Grignard processes is the always present fire hazard due to the explosive vapors[10] of the commonly used solvent, ethyl ether.

The purpose of my project is the elimination, or at least reduction of the danger of working with this flammable, volatile liquid, without seriously inhibiting the vigor of the reaction. It is well known that higher alkyl ethers as well as aromatic ethers are less volatile and considerably less hazardous than ethyl ether. Specifically then, I was interested in establishing whether or not some or all of these different ether types could be used, instead of ethyl ether, to make a Grignard reagent.

Historical

A thorough search of *Chemical Abstracts, The Journal of The American Chemical Society,* other periodicals, and various reference books disclosed a great number of reports on the Grignard reactions. Some dealt with the preparation of the compounds themselves, most of them covered the

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[1] E.g. rubber vulcanization. See Midgley, Henne and Shepard. *Journal of the Amer. Chem. Soc.* 56:1156 (1934).

[2] D. F. Wilcock, "Silicone Oils."

[3] "DC Silicones" (Dow Corning Corp. 1947).

[4] P. C. Servais, "New Developments in Silastic."

[5] "Silicone Rubber" (General Electric Corp.).

[6] Krause and co-workers, *Berichte,* 52:2165 (1919); *ibid.,* 53:173 (1920); *ibid.,* 54:2060 (1921); *ibid.,* 55:888 (1922).

[7] Moeller and Pfeiffer, *ibid.,* 49:2443 (1916).

[8] Goddard, *J. Chem. Soc.,* 123:1161 (1923).

[9] Austin, *J. Am. Chem. Soc.,* 54.3726 (1932).

[10] Explosive range for ethyl ether in air (by volume) from 1.7 per cent to 48 per cent — a very wide range.

reagents' numerous applications to synthesis. I was not able to find, however, any article comparing the effect of solvent ether structure and the influence of mixtures of ethers and high-boiling cyclic hydrocarbons on the preparation of Grignard compounds.

Although Spencer,[11] Bruhl,[12] Malmgren,[13] Schlenk, Jr.,[14] and their associates have shown that a number of Grignard compounds can be prepared without the use of ethyl ether, or even without any solvent, these methods are in general inefficient. Formation of unwanted by-products,[15] and the excessive time,[16] heat[17] or catalysis required make them impractical.

Chelintsev[18] proposed to make Grignard reagents in benzene solution in the presence of traces of the catalyst dimethylaniline. He corroborated previous evidence that materials like diethyl ether, anisole, pyridine, and tertiary amines in general made reaction between magnesium and alkyl halides much easier to perform. While this method has some merit, the high flammability of the volatile benzene, coupled with its low flash and boiling points,[19] make this process almost as hazardous as that using ethyl ether.

Research on catalysts for Grignard reaction probably resulted from the necessity of having to prepare reagents from inactive chlorides, complex halides and sluggish solvents. Iodine crystals,[20] "activated" magnesium,[21] previously prepared Grignards,[22] tertiary amines,[23] and various other organic[24] and inorganic[25] compounds have been used to accelerate the formation of Grignard reagents.

I have attempted to compare the relative catalytic efficiency of iodine, previously prepared Grignard compounds, "activated" magnesium, xylene and anisole in order to determine which catalysts are most suitable for starting Grignard reactions in solvents other than ethyl ether. This type of comparative study could not be found in the literature.

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[11] a Spencer and Stokes, *J. Chem. Soc.*, 93:68 (1908).
b Spencer and Crewdsob, *ibid.*, 93:-1822 (1908).
c Spencer, *Berichte*, 41:2302 (1908).

[12] Bruhl, *Berichte*, 36:668 (1903); *ibid.*, 37:746 (1904).

[13] Malmgren, *ibid.*, 36:2608 (1903).

[14] W. Schlenk, Jr., *ibid.*, 64:739 (1931).

[15] a P. Schorigin, W. Issaguljanz, A. Gusseva, *ibid.*, 66:1426 (1933).
b Kahan, *Trans.*, 93:133 (1908).
When magnesium is reacted with alkyl halide without any solvent, a secondary reaction takes place forming an R-R type hydrocarbon as by-product:
(1) $RX + Mg \rightarrow RMgX$
(2) $2RMgX + Mg \rightarrow R\text{-}R + MgX_2$

[16] It took Schlenk, Jr. two months for his reaction which took place in benzene without use of heat or catalysis; even after that time, some halides did not react, e.g. CH_3I.

[17] Spencer learned that the lower alkyl halides reacted with magnesium only when the two were heated in a sealed tube to about 270°C.

[18] Chelintsev, *Berichte*, 37:4534 (1904).

[19] Benzene — flash pt.11°C, b.p. 80°C; ethyl ether-flash pt.-41°C, b.p. 34°C.

[20] It is common for organic experimental texts to suggest addition of iodine crystals to a sluggish Grignard in order to start it.

[21] Baeyer found that if magnesium were first "activated" by warming it with iodine and the resulting gray powder were used instead of the pure metal, reactions with difficult alkyl halides could be greatly facilitated. The "activated" magnesium is probably a mixture of magnesium powder and magnesium subiodide. It turns from a dull gray to a deep brown after prolonged exposure to air. See Baeyer, *Berichte*, 38:3759 (1905).

[22] Sachs and Ehrlich, *ibid.*, 36:4296 (1903).

[23] W. Chelintsev, *ibid.*, 37:4539 (1904); *ibid.*, 38:3664 (1905); *ibid.*, 39:773, 1674, 1682, 1688 (1906); *ibid.*, 40:1487 (1907); *Comt. Rend* 144:887 (1907).

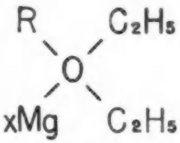
[24] E.g. xylene, pyridine, dimethylaniline, anisole, alkyl halides, ketones.

[25] E.g. metallic halides such as aluminium chloride.

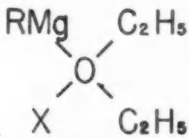
Theoretical

Chelintsev[26] has suggested that ether's role in the preparation of a Grignard salt is to dissociate the alkyl halide so that it will react with magnesium. The ether appears to form an oxonium complex with the halide:

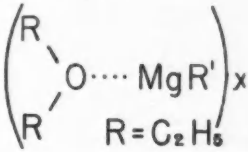
When the reaction takes place in pure ethyl ether, this complex combines with the magnesium metal, forming a new oxygen-containing etherate, for which the following formulae have been suggested:



Grignard[27]

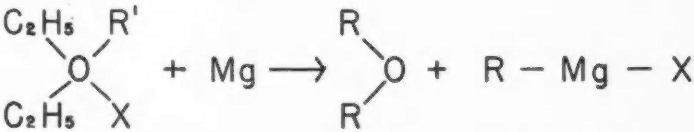


Baeyer[28] Villiger



Werner

This compound is soluble in ether and may be isolated.[29] When the Grignard reaction takes place in a cyclic hydrocarbon containing only a trace of ether, the alkyl halide again forms an oxonium complex with the ether which, however, then reacts with the magnesium metal forming the pure alkyl magnesium halide and regenerating the ether:[26]



The pure alkyl magnesium compound is insoluble in the hydrocarbon and settles in the form of whitish flakes. These insoluble Grignard compounds are called "individual" Grignards.

When no solvent is used, dissociation of the halide is caused, in my opinion, by the relatively high temperature at which reaction must be started. This explains why Spencer[30] had to heat his alkyl halide and magnesium to 270°C.

I have attempted to prepare magnesium organic salts in both ethereal

[26] Chelintsev, *Berichte*, 38:3664 (1905).
[27] Grignard, *Bull. Soc. Chim.* (3) 29:944 (1903), *Comt. rend.* 13:1262 (1903).
[28] Baeyer and Villiger, *Berichte*, 35:-1201 (1903).
[29] When ethyl iodide reacts with magnesium metal in ether and the product is heated under low pressure in a current of dry hydrogen, the ether is not completely driven off and a compound with the formula $C_2H_5MgI.(C_2H_5)_2O$ remains.

[30] See footnotes 11 and 17.

solutions and in benzol-like solvents. I wanted to see whether or not an ether which is entirely aliphatic, an ether which is mixed aliphatic and aromatic, a straight aromatic ether, and a poly-ether would produce the required oxonium complexes and make possible the formation of Grignard reagents. I have tried to determine how addition of a liquid of the benzene series, such as xylene, to these higher boiling ethers would affect the formation of Grignard reagents.

Experimental

My experiments are divided into two groups. The first section covers the effect of solvent ether structure on the synthesis of Grignard compounds. The second deals with the use and influence of catalysts on their synthesis in those cases where the ether structure has been modified.

Section one: Four types of solvent ethers have been tested. Butyl ether represented the alkyl ether series. Diethyl carbitol, the diethyl ether of diethylene glycol, was tested as a typical aliphatic poly-ether. Anisole, phenyl methyl ether, was employed as a characteristic mixed aryl-alkyl ether. Phenyl ether, which I could obtain only in the form of the heat conductor Dowtherm A (76 per cent by volume phenyl ether, 24 per cent diphenyl), represented the diaryl ethers. These ethers were selected because of their high boiling points and, in general, their relatively high flash points, especially as compared with ethyl ether.

I had planned work with additional solvents such as ethylal and dioxane, but the chemicals could not be procured in time.

Calculated quantities of solvents, metal, and halide were employed. Because of the high cost of chemically pure alkyl halides[31] my experiments were carried out mostly on test tube scale. I had planned to use three methods to measure the yields of the reactions and the ease with which they were started: (1) determination of the amount of metallic residue, (2) titration of the hydrolytic products of the Grignard compound, (3) measurement of the temperature at which reaction took place.

Because my experiments were generally on a small scale, exact quantitive determination of the magnesium residue proved rather inaccurate and, in the case of the insoluble, "individual" Grignard compounds, undesirable. Moreover, lack of semi-microchemical apparatus caused me to abandon my plan of titrating hydrolyzed Grignard reagent with dilute acid. However, temperature measurements within range of my thermometer (which read to only 110°C but could be estimated to 135°C) were carefully recorded.

Solvents and halides were dried carefully. In order to dry all liquid reactants, sodium wire was added to the liquids and the mixtures were allowed to stand. Those which showed high water content were distilled and again treated with sodium. Absolute, Reagent grade ethyl ether was tested for peroxides by addition of ferrous sulfate followed by potassium sulfocyanide.[32] CP magnesium powder was used instead of ribbon or chips because of its greater reactivity.

Table I

My findings with unmixed ethers are tabulated below. In the procedure that follows, .02 moles of the ether

[31] The lower alkyl bromides and iodides retail from $4.50 to $8.00 per pound.

were mixed with .01 mole of alkyl halide in a test tube, and about 270 milligrams[33] of magnesium powder added. In the case of Dowtherm A, the necessary adjustment was made to compensate for the 24 per cent diphenyl present. The liquids were heated on an oil bath and temperatures at which reactions occurred, were carefully recorded. Figures below are averages of several readings.

ETHER				HALIDE		TEMPERATURE °C		YIELD[34]
NAME	FORMULA	B.P.	WEIGHT (grams)	FORMULA	WEIGHT (grams)	without catalyst	with catalyst	
Diethyl ether	$(C_2H_5)_2O$	34.6	1.48	CH_3I	1.42	28	21 (MgI)	A
				C_2H_5I	1.56	34	24 (G)	B
				$CH_3CHBrCH_3$	1.23	34	21 (MgI)	A
Dibutyl ether	$(C_4H_9)_2O$	142.4	2.60	CH_3I	1.42	n.r.[36]	21 (MgI)	A
				C_4H_9Br (n)	1.37	75	60 (I)	B
Diethyl carbitol				CH_3I	1.42	n.r.[36]	101 (MgI)	D[37]
	$(C_2H_5OC_2H_4)_2O$	188	3.24	C_4H_9Br (n)	1.37	188?	188? (G)[37]	D
Anisole	$C_6H_5OCH_3$	154 to 155	2.16	CH_3I	1.42	n.r.[36]	41 (MgI)	B
				C_4H_9Br (n)	1.37	122	62 (G)	C
Diphenyl as Dowtherm A	$(C_6H_5)_2O$	259	3.40	CH_3I	1.42	n.r.[36]	41 (MgI)	C
				C_4H_9Br (n)	1.37	n.r.	98 (G)	B

TABLE II

The following table lists results obtained when .01 mole of alkyl halide was reacted with about 270 milligrams[33] of magnesium powder in the presence of .01 mole of a high boiling ether and 1.06 grams (.01 mole) of xylene. These experiments were car-

ETHER				HALIDE		TEMPERATURE °C		YIELD[34]
NAME	FORMULA	B.P.	WEIGHT (grams)	FORMULA	WEIGHT (grams)	without catalyst	with catalyst	
Diethyl ether	See Table I		0.74	CH_3I	1.42	61	26 (MgI)	A
				C_2H_5I	1.56	82	34 (MgI)	B
Dibutyl ether			1.30	CH_3I	1.42	n.r.[36]	44 (MgI)	B-A
Anisole			1.08	CH_3I	1.42	n.r.[36]	38 (MgI)	B-A
				C_4H_9Br (n)	1.37	132	92 (G)	B
Diphenyl ether as Dowtherm A			1.70	CH_3I	1.42	n.r.[36]	76 (MgI)	B-C
				C_4H_9Br (n)	1.37	n.r.	98 (G)	B-C

[32] Presence of peroxides in the ether would bring about oxidation of the ferrous ion to ferric which would then react with KCNS forming red $Fe(CNS)_6$.

[33] About 10 per cent of magnesium over the calculated amount was used to keep an excess of RX from forming R-R by-products.

[34] The yield was visually estimated and was graded A, B, C, or D in decreasing order of yields.

[35] The catalyst used is indicated in parentheses after each temperature reading. I—iodine; G—previously made Grignard; MgI—"activated" magnesium.

[36] Failure of reaction to start at high temperatures might be partially caused by the boiling away of the methyl iodide (B.P. 42.4°C) despite an air condenser.

[37] These diethyl carbitol Grignards were very sluggish and usually died out after a few minutes. The yield was atrociously low.

ried out in order to determine the influence of a typical benzene-like compound when mixed with the ethereal solvents in the preparation of Grignard compounds.

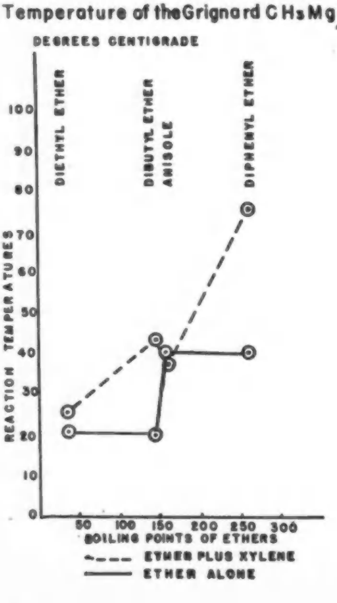
Table III

In experiments devised to learn reaction temperatures with mixtures of ethers, the following findings were obtained:

Ether: Name	Ether: Formula	Ether: B.P.	Ether: Weight (grams)	Halide: Formula	Halide: Weight (grams)	Temperature °C: without catalyst	Temperature °C: with catalyst	Yield[34]
Anisole	See Table I		1.08					
Diphenyl ether as Dowtherm A			1.70	CH_3I	1.42	n.r.[36]	51 (MgI)	C
Anisole			1.08					
Ethyl ether			.74	$CH_3CHBrCH_3$	1.23	81	62 (MgI)	B

The relative efficacies of the various ethers used in the present work, both alone and admixed with xylene, are illustrated in the accompanying graph.

The Effect of Xylene on the Reaction Temperature of theGrignard CH_3MgI



Section two: It has been shown in Tables I and II that various catalysts help in starting Grignard reactions utilizing certain high-boiling ethers. The comparative effectiveness of several catalysts when used in ethyl ether Grignards is shown in the following. A molecular proportion of isopropyl bromide was reacted with an equivalent of magnesium powder in the presence of two equivalents of ethyl ether. A trace of the catalyst to be tested was then added, and the mixture, if it had not already started to combine, was warmed in an oil bath.

Table IV

Catalyst	Reaction temperature °C
None	34
Iodine crystals	33
Previously made Grignards	31
Magnesium iodide ("activated" magnesium)	21
Anisole	51
Xylol	59

By analogy, it is possible that these data will be of further use in establishing the best catalysts for the nonvolatile ether Grignard reactions. The

limited investigations of Tables I and II support, in so far as they go, the observation in Table IV.

Conclusions

1. It has been shown that certain relatively non-volatile ethers can be used in Grignard reactions to replace the commonly used flammable ethyl ether. These are dibutyl ether, anisole, and diphenyl ether.

2. The poly-ether diethyl carbitol was found to be ineffective for the purpose. The sample of this chemical which was used was of doubtful purity, so this compound will be reinvestigated at the next opportunity.

3. It has been shown that the following Grignard catalysts are quite effective and that their effectiveness decreases in the order listed: "activated" magnesium, previously made Grignard compounds, and iodine crystals. This work was done in ethyl ether but the conclusions are probably applicable to cases involving solvents such as anisole, diphenyl ether, and dibutyl ether.

Lack of time and equipment made it impossible to carry out my investigations to the desired degree. Several interesting and promising results have been obtained but the field is far from being exhausted. I intend to continue my work on the poly-ethers and to study the compounds of the methylal group in relation to their applications to Grignard formation.

The endless possibilities of organo-metallic chemistry, especially in relation to their recently suggested[38-39] connections with hemoglobin and photosynthesis, offer an excellent territory for further research.

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[38] a Wilstaetter, *Annalen*, 350:64 (1906).
b Ruben and Kamen, *J. Am. Chem. Soc.*, 62:3451 (1940).

[39] Kunz and Kres, *Berichte*, 60:367 (1927).

Silicones and Silanes

by Ronald Charles Breslow, 16.
Rahway High School, Rahway, N. J.

➤ Although recently much work has been done in the field of silicones, little has been done in the investigation of the silicon hydrides and their *inorganic* derivatives. Some time ago I became interested in the chemistry of these compounds, which are analogous to organic compounds, but contain silicon instead of carbon. I have since done considerable research and some experimentation in this field.

The only silicon hydrides known are the straight chain compounds. Therefore, all known silicon hydrides can be named as derivatives of the straight chain saturated hydrides, called "silanes."

The most common silane is di-silane, Si_2H_6. The other silanes and some unsaturated silicon hydrides occur in small concentrations when the silanes are prepared by the standard method.

When I decided to do some research into the chemistry of the silanes, the first problem was how to prepare them. I decided that preparation of a metallic silicide and hydrolysis of that silicide would be theoretically workable. Research dis-

closed that the heating of magnesium with silica and the subsequent decomposition with acid of the resulting magnesium silicide mixture had been the method of most workers. My primary interest, however, is in the theoretical side of silicane chemistry. Therefore, my first investigation was into the mechanism of the decomposition reaction.

As the previous workers had used aqueous acids in the reaction with magnesium silicide, I wished to discover whether water is necessary in this reaction. I first prepared the magnesium silicide and tested it with aqueous hydrochloric acid. Silanes were given off, as I could easily see since they explode on contact with air. Next I prepared a solution of hydrogen bromide in absolute ether by adding to the ether some water and an excess of phosphorus tribromide. There was no apparent reaction when this was added to the silicide. Fearing that the absence of water had resulted in non-ionization of the hydrogen bromide, I attempted the reaction

$$Mg + 2HBr(\text{anhydrous ether}) \rightarrow H_2 + MgBr_2$$

As this reaction proceeded readily, it is obvious that the hydrogen bromide was ionized in absolute ether. Therefore, the only place for the water is in the formation of an intermediate product or as a catalyst for the reaction, since, judging from the end products, the reaction seems to be

$$Mg_2Si + 4HBr \rightarrow 2MgBr_2 + (SiH_4)\ ;\quad 2SiH_4 \rightarrow Si_2H_6 + H_2$$

Some mention of the formation of an intermediate product is made in the literature.

My big problem in all my experiments has been lack of the proper equipment. Alfred Stock, who has done most of the work in the field of silanes, was able to test the gases "in vacuo" by first condensing them with liquid air, thus ridding them of the troublesome hydrogen gas which is always a by-product of their preparation. I have yet to devise a method of eliminating this impurity at the room temperature at which lack of liquid air forces me to work. However, I have devised another method which enables me to analyze with a fair degree of accuracy the gases which are formed by the acidification of magnesium silicide. Percentage of silicon per unit volume is a relatively simple determination, as the gas in any given quantity can be aspirated through KOH. This decomposes the silanes by the reaction

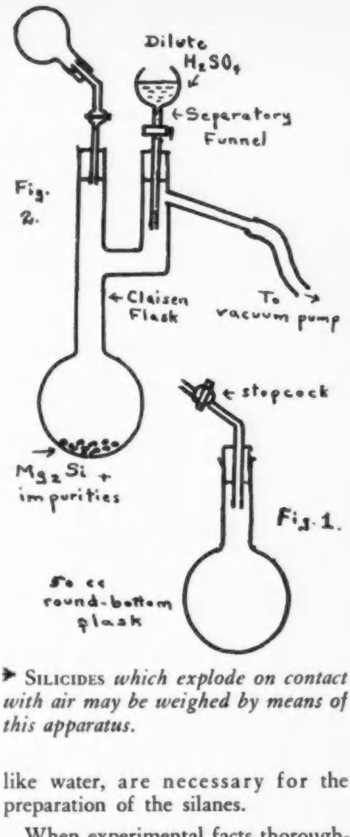
$$4KOH + Si_2H_6 + 2H_2O \rightarrow 2K_2SiO_3 + 7H_2$$

SiO_2 can then be precipitated from the solution with acid and weighed. Although Si_2H_6 is used in the equation, any silane reacts with the alkali solution, although in the case of other silanes the yield of hydrogen is different.

The other determination necessary to calculate the percentages of the various gases present in the mixture is the density of the mixture, from which can be calculated the average molecular weight. The fact that the gases explode spontaneously in air makes this determination slightly difficult, but I use the following method, which has proved satisfactory. I fit a small flask with a stopper and a stopcock (figure 1), evacuate the apparatus, and weigh it. Next I equip the curv-

ed neck of a Claisen flask with a separatory funnel, place the silicide in the Claisen flask, fit the evacuated small flask, with stopcock closed, to the other neck of the Claisen flask, and evacuate the Claisen flask by means of its delivery tube (figure 2). Adding acid through the separatory funnel, I open the stopcock of the small flask and allow air to enter the Claisen flask through the separatory funnel. This forces gas into the small flask at atmospheric pressure, and the flask is quickly closed off by means of the stopcock and weighed. The volume taken is determined by re-evacuation and filling with distilled water, the apparatus again being weighed, as the density of water is known. I have found no explosion when the air enters, although of course inert atmosphere could be used. I used this method for determining the average molecular weight of the gas from a sample of silicide I had prepared. After decomposing the magnesium nitride present with alkali water, I performed the determination, making all corrections for temperature, pressure, buoyancy of air, etc., using a good analytical balance. The density I found to be 1.441 grams/liter. From this I calculated the average molecular weight to be 32.3, and the percentage of silanes was about 58%.

In the future I shall investigate the theoretical side of the preparation further by preparing pure Mg_2Si, using a mixture of magnesium and silicon heated *in vacuo*. The "silicide" now used contains, in addition to Mg_2Si, at least some MgO Mg_3N_2, $MgSiO_3$, and SiO_2. It will be of interest to see whether these substances,



➤ SILICIDES *which explode on contact with air may be weighed by means of this apparatus.*

like water, are necessary for the preparation of the silanes.

When experimental facts thoroughly explain the fundamental reactions of the silanes I can start working toward my real goal — the preparation of aromatic silicon hydrides. I may never prepare these unknown substances, for silicon, unlike carbon, is unstable in the double linkages which characterize aromatic compounds. However, resonance, the stabilizing factor in carbon chemistry, may prove

to be the stabilizing factor in silicon chemistry and enable me to prepare a whole family of compounds which do not now exist. Such a discovery would more than justify the repeated attempts at preparation I will make before conceding that the chemistry of the silicon hydrides does not have the tremendous unexplored potentialities I now envision.

On Substituted Amino-nitrobenzenes

by Charles Frederick Wilcox, Jr., 17.
Greenwich High School, Greenwich, Conn.

➤ The correlation of physical properties to molecular structure has deeply interested me from my earliest readings in organic chemistry. Thus it was with great pleasure that I read that J. J. Blanksma and others had prepared various substituted amino-nitrobenzenes, many of which had an abnormal sweetness, for with these compounds I would be able to test easily the changes in sweetness caused by corresponding structural variations.

I decided that first I would have to duplicate the previous work in order both to check the results and to gain skill in preparing such compounds. Having done this I then would be able to make my changes and interpret the results accurately.

I noticed that the sweetest series is the alkoxy derivatives. I therefore planned to prepare thio-alkoxy-amino-nitrobenzenes by means of the following procedure in order to ascertain the effect of the replaced oxygen.

$$CS_2 + KOH + ROH \rightarrow H_2O + RO\overset{\overset{S}{\|}}{C}\cdot SK$$

$$ArN_2Cl + KS\cdot\overset{\overset{S}{\|}}{C}\cdot OR \rightarrow KC + N_2 + ArS\overset{\overset{S}{\|}}{C}\cdot OR$$

$$ArS\overset{\overset{S}{\|}}{C}\cdot OR \xrightarrow{\text{HEAT}} ArSR$$

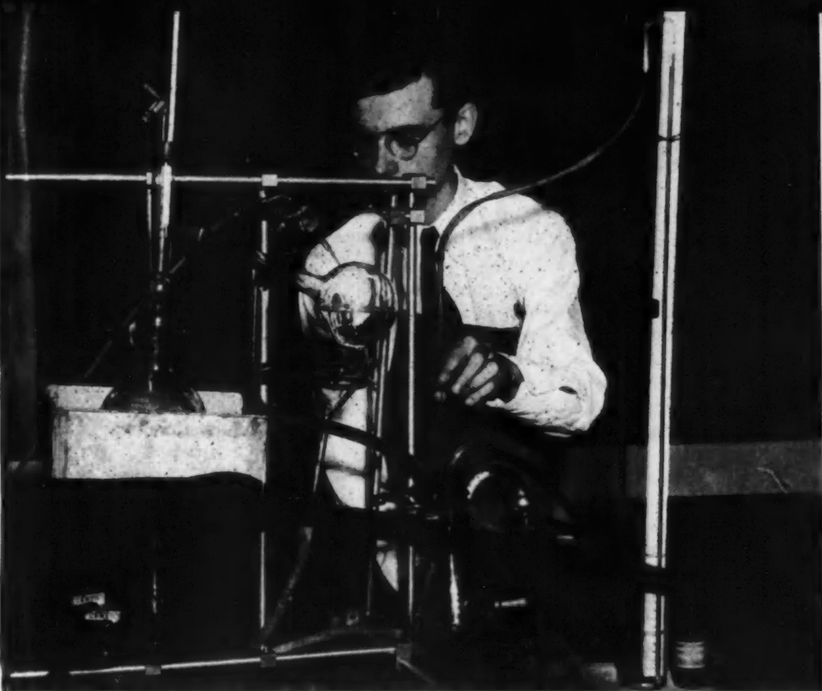
I also planned to determine the difference caused by changing the basic ring structure which in this case would be from benzene to napthalene or some more complex group. In that direction I have already prepared some substituted amino-nitronapthalene compounds. However, as yet, these efforts have not resulted in conclusive evidence.

Following my plan, most of my time has been spent in preparing compounds already made by other workers. Some of the prepared compounds are listed below along with their relative sweetness.

I present here the preparation of two representative compounds, 2-amino-4-nitrotoluene and 2-amino-4-nitro-1-n-propoxybenzene. The other compounds may be prepared in an analogous manner. The preparations given include my modifications and also clearer directions in cases where original reference had been ambiguous.

Preparations

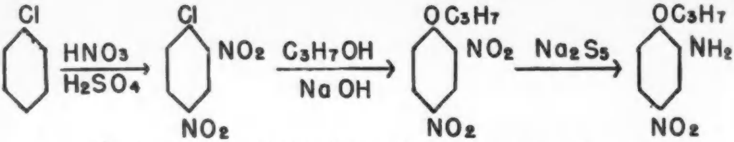
➤ To make 2-amino-4-nitro-1-n- propoxybenzene, 175 g. of conc. nitric acid were placed in a liter flask. To this were added 175 g. of conc. sulfuric acid. After this had been cooled to 2 degrees, it was added cautiously



➤ IN HIS HOME *laboratory, Charles F. Wilcox, Jr. is trying various substitutions in the amino-nitrobenzene molecule to find out which resulting compound has the sweetest taste. One of his preparations is so many times sweeter than sugar that, although it is very slightly soluble, its water solution seems to him to taste just right!*

Relative Sweetness of the Compounds Prepared

2-amino-4-nitrofluorobenzene	40
2-amino-4-nitrochlorobenzene	400
2-amino-4-nitrobromobenzene	800
2-amino-4-nitroiodobenzene	1250
2-amino-4-nitrotoluene	330
2-amino-4-nitrobenzoic acid	25
2-amino-4-nitro-1-methoxybenzene	220
2-amino-4-nitro-1-ethoxybenzene	950
2-amino-4-nitro-1-n-propoxybenzene	4100



➤ PREPARATION *of 2-amino-4-nitro-1-n-propoxybenzene.*

to 113 g. of mono-chlorobenzene with good agitation, the temperature being kept below 5 degrees by external cooling. After all had been added the temperature was maintained at 5-10 degrees for an hour. Then the temperature was slowly raised to 50 degrees and kept there for one hour. With good stirring 350 g. of conc. sulfuric acid were then dropped in and the mixture finally heated to 115 degrees for half an hour. After cooling to about 55 degrees the reaction mixture was poured into ice water, where it solidified immediately. The mother liquor was poured off and the dinitro-chlorobenzene washed free of acid. Yellow crystals; M.P. 51 degrees.

8.4 g. of sodium hydroxide were dissolved in 210 ml. n-propyl alcohol. This was added dropwise with good stirring in the course of two hours at a temperature of 70 degrees to a solution of 41 g. of 2, 4-dinitrochlorobenzene in 405 ml. n-propyl alcohol. The temperature was maintained at 70 degrees for an half an hour longer. The mixture was then cooled to room temperature and the sodium chloride which had separated was filtered off. The n-propyl alcohol was distilled off in vacuo (15 mm. pressure). To the residue was added ether and 1% sodium hydroxide solution, the latter in view of the 2, 4-dinitrophenol formed by the action of water, a product of the main reaction, on the 2, 4-dinitrochlorobenzene. After shaking well, the two layers were separated. The ethereal layer was washed once with water and dried over anhydrous sodium sulfate. The ether was distilled off and left an oil behind. This can be crystallized by cooling in an ice-chest. M.P. 30-32 degrees.

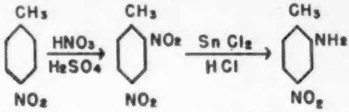
1 g. of 1-n-propoxy-2,4-dinitrobenzene was emulsified with 150 ml. warm water. To this was added in the course of one half an hour 10 ml. of sodium polysulfide solution prepared as follows: 5 g. sodium hydroxide and 1 g. sulfur were added to 15 ml. water; the mixture was boiled until most of the sulfur had been dissolved; the solution was filtered, the filtrate being used as above. The temperature was maintained at 70 degrees for half an hour. On cooling an oil was formed on the surface of the water. This was dissolved in ether and the ether layer separated. The ether was then evaporated. The 2-nitro-4-amino-1-n-propoxybenzene formed as a by-product may be separated as follows: the material obtained above is dissolved in hydrochloric acid, warmed with a little animal charcoal, and filtered. When cooled 1-n-propoxy-2-amino-4-nitrobenzene separates as orange crystals. M.P. 49 degrees. Although its solubility in water is very low its great sweetness (4100 times sweeter than sugar)

makes a water solution taste just right.

Second Preparation

➤ To PREPARE 2-amino-4-nitrotoluene, 18 g. of fuming nitric acid (freshly prepared) were added to 30 g. of conc. sulfuric acid. To this mixture 14 g. of p-nitro-toluene were added slowly with frequent cooling. After all had been added a funnel was placed in the flask stem down serving both as a condenser and vent for any gases formed. The flask was heated on a boiling water bath for half an hour. It was cooled nearly to room temperature and then poured into 500 ml. of ice water. Crude 2, 4-dinitrotoluene separated immediately. This was collected on a funnel, washed with water and recrystallized from hot methyl alcohol affording fine needles. M.P. 70.5 degrees.

10 g. of 2, 4-dinitrotoluene were dissolved in 50 ml. of methyl alcohol



➤ PREPARATION *of 2-amino-4nitrotoluene.*

and added to 100 ml. water. 30 g. of stannous chloride dissolved in hydrochloric acid were added. The mixture was refluxed for an hour accompanied by a color change from clear to orange-red. The 2-amino-4-nitrotoluene was separated. Pure 2-amino-4-nitrotoluene is 330 times sweeter than sugar; M.P. 107 degrees.

My work is not yet complete but I will finish, as far as is possible, these investigations before entering college. It will not then be simply forgotten for I consider this work to border on basic questions. I feel strongly that someday the research I have done and that I intend to do will prove beneficial to humanity.

Extraction of Gold from Sea-Water

by GEORGE CAMAMIS, 17.
New Brunswick Senior High School, New Brunswick, N. J.

➤ FOR THE PAST two years I have been greatly interested in the extraction of gold from sea-water or other natural salt-water bodies such as the Great Salt Lake in Utah. Recently I have worked extensively in my laboratory on sea-water from the Atlantic Ocean and have obtained fairly good results. It is a known fact that gold is present in sea-water in very small amounts*; and for my own curiosity I proved it by the following method:

To about 200 c.c. of sea-water add 300 mg. of pure ferrous sulfate dissolved in distilled water and acidulated by addition of a few drops of dilute hydrochloric acid. The solution is heated in a porcelain dish over a low flame until a film of ferric oxide is produced. This precipitate is collected, rinsed in distilled water and placed in a clean evaporating dish.

To the precipitate in the evapor-

* E. Sonstadt, an English chemist, proved in 1879 that gold is present in sea-water in minute amounts as auric acid (H_3AuO_3).

ating dish is added strong chlorine water and it is heated almost to dryness. To the remaining liquid is added stannous chloride test reagent. A characteristic blue color results, proving the presence of gold.

In order to be sure that my apparatus and reagents did not contain any gold that would give a blue color with stannous chloride solution, I performed the same experiment on distilled water. The results were negative, verifying my first conclusion.

By the use of electrometric analytical methods, chemists recently showed that the amount of gold in the sea-water of the Atlantic Ocean is between 3 and 4 mg. to the ton of the sea-water. Since then chemists at Columbia University have tried to recover gold from sea-water on a large scale by electrolysis. The experiments at Columbia failed because by electrolysis they formed coloidal gold which cost too much to convert into metallic gold.

Another attempt was made by a German company before the war. They tried to precipitate gold by using ferrous sulfate and stannous chloride as precipitating agents. Failure resulted when no appreciable amounts of gold were precipitated.

Since it was my desire to extract gold from sea-water, I began to experiment on my own. I started by trying all kinds of precipitating agents on sea-water and finally found that it is possible to use barium aurate. [$Ba_3(AuO_3)_2$]

Barium chloride will also precipitate all soluble sulfates which are inevitably present in sea-water. This makes separation of the barium aurate precipitate from the sulfate precipitates difficult. I have found, however, that barium chloride can only precipitate barium aurate in an alkaline solution of pH 7; the sulfates can be precipitated off without precipitating any barium aurate by making the sea-water acid to pH 2. Using these facts I devised the following method to extract a very minute amount of metallic gold from sea-water:

Bring several gallons of sea-water to pH 2 by use of hydrochloric acid and add about a gram of barium chloride. Allow the precipitate formed to settle for several days, after which pour off the clear sea-water into another container and bring it up to pH 7 with sodium hydroxide solution. This time add only 20 mg. of barium chloride and allow the precipitate of barium aurate to settle. The equation for the last reaction being:

$$3BaCl_2 + 2H_3AuO_3 \rightarrow 6HCl + Ba_3(AuO_3)_2$$

After allowing the precipitate of barium aurate to settle a few days, collect it and wash it from impurities with distilled water. Mix the dried barium aurate precipitate with lead as a reducing agent and borax as a flux. Heat the mixture on charcoal block with a blowpipe flame until a small glass bead is formed. The equation for the reaction being:

$$Ba_3(AuO_3)_2 + 3\ Pb \rightarrow 3\ BaO + 3\ PbO + 2\ Au$$

In the reduction reaction above free gold is formed and is locked up in a glass bead of borax which was used as a flux in the reduction. Also throughout the bead mixed with the free gold are the other two products

of the reduction reaction, barium oxide and lead oxide. In order to remove the free gold it is necessary to crush the bead into a fine powder and to mix the powder thoroughly with mercury. The mercury comes in contact with the small gold particles and forms an amalgam. By collecting the mercury and distilling it off, a very thin film of gold remains behind.

The amount of gold I recovered by the method described above was only about 15 micrograms. But by calculating the amount of sea-water that I used and the amount of gold recovered, I found that I had precipitated by percentage almost as much gold as Fritz Haber, the German chemist, who succeeded in obtaining .154 grains of gold to the ton of sea-water.

On a commercial basis sea-water can be received at high tide in large tanks each holding hundreds of tons of sea-water. The precipitation processes would be carried out in these tanks. The barium aurate precipitate would be collected from the bottom, carried to a furnace where the gold would be reduced with lead, and the free gold removed with mercury. The mercury then would be distilled off and the free gold collected. Although this sounds very easy, there are many chemical engineering problems which would arise and offer much difficulty.

After my college training, I would like to analyze many of the natural salt water bodies of the world for their gold content and work out a commercial process that could profitably extract the gold. It seems to me that the Great Salt Lake in Utah would contain a high percentage of gold since it was formed by rivers flowing through regions which contain gold ores.

Chemiluminescence

by Jerry Blair Miller, 17.
Lincoln High School, Canton, Ohio.

➤ Although the process of chemiluminescence is known and brought close to all of us by the firefly and glow-worm few people recognize it as such. Chemiluminescence in all its forms has bewildered and fascinated man since the beginning of time. Even today people are amazed at the bright, shining trail sometimes left by boats, amazed by the glowing tree trunk and even the harmless firefly.

Science has come a long way on the search for understanding of this process. One of the initial steps was to reproduce the effect in a test tube. From the first, difficulties were encountered due to the unpleasant materials necessary to handle. For instance the Wedekind reaction between chlorpicrin (a lachrymator) and phenylmagnesium bromide in ether or various reactions of Grignard compounds (unstable and involving the use of ether solutions) are but two examples of the difficult reagents which had to be handled.[1] However, the discovery of the compound, 3-aminophthalhydrazide ("luminol"),

has provided a simple and safe way to demonstrate chemiluminescence.

The author's purpose in these luminol experiments was to determine the effect if any of: (1) varying amounts of reagents involved, (2) other oxidants, (3) organic compounds, (4) bases or basic salts and (5) acids or acidic salts.

A standard solution was prepared consisting of:

.05 gm. 3-aminophthalhydrazide
5 c.c. 5% potassium hydroxide
5 c.c. 3% hydrogen peroxide
.1 gm. potassium ferricyanide
Water to make 250 c.c.

The experiment was then set up as follows:

Variable + 10 c.c. H_2O

0 gm.	.05 gm.	.1 gm.	.2 gm.	.4 gm.	.8 gm.
1	2	3	4	5	6

Test tubes

20 c.c.	20 c.c.	20 c.c.	20 c.c.	20 c.c.	20 c.c.
1	2	3	4	5	6

Luminol solution minus the variable

The author's original intent was to measure the foot-candle light initially produced and again after 5 minutes but after both the available light meters, a Weston photographer's meter and a General Electric meter, proved too insensitive it became necessary to make only a relative estimate.

Variable Potassium Hydroxide

An extremely faint luminescence was observed even in the complete absence of potassium hydroxide; the light increased very greatly in tube No. 2 and continued to increase. It was observed, however, that the difference in light between the tubes and length of luminating time both became less as the KOH concentration went up. No. 3 tube gave the best all-around light (bright light, long luminating time).

Variable Potassium Ferricyanide

Precisely the same results were obtained by varying the amount of potassium ferricyanide. Tube No. 3 again provided the best illumination.

Variable Hydrogen Peroxide

Due to the necessity of using 3 per cent H_2O_2 in this part it, of course, required more than 10 c.c. to obtain the desired weight of H_2O_2. As a result the variable tubes were made to contain 20 c.c. of solution.

The results with this variable differed considerably from those of the others. Tube No. 1 luminesced very much brighter than any of the previ-

[1] Ernest H. Huntress, Lester N. Stanley, and Almon S. Parker, "The Oxidation of 3-aminophthalhydrazide (Luminol) as a Lecture Demonstration of Chemiluminescence," *J. Chem Education*, Mar., 1934 142-45.

Action of Other Oxidants

Oxidants	With potassium ferricyanide omitting H_2O_2	With H_2O_2; omitting potassium ferricyanide
1. $KMnO_4$	Extinguishes light	Extinguishes light
2. $KClO_3$	———	———
3. $NaNO_3$	———	———
4. $(NH_4)_2Cr_2O_7$	Extinguishes light	Extinguishes light
5. I_2 in alcohol	Emits dim light, sometimes intensified by violent shaking; iodine particles glow	Emits dim light; iodine particles glow
6. ferric ammonium sulfate	momentary light and then extinguished	momentary light and then extinguished
7. ferrous ammonium sulfate	Same as ferric salt	Same as ferric salt
8. sodium ferricyanide	———	———

ous No. 1 tubes. No. 2 was slightly brighter and from there on up the light was extinguished. This is explained, I think, by the action of No. 1 tube. At the beginning all the tubes were like No. 1, i.e., luminescing rather brightly. They remained so for about 5 minutes before the variable tubes were added and apparently oxidation had proceeded far enough so that the addition of a further oxidant, in the form of H_2O_2, was sufficient to complete the oxidation instantly.

Bases or Basic Salts

1. NH_4OH	Very dim
2. Na_2CO_3	Rather bright
3. $(NH_4)_2CO_3$	Very dim
4. NaOH	As good as KOH

With the exception of NaOH none were bright enough to replace KOH. NaOH, however, seems just as good.

Acids or Acidic Salts

Nine reagents were tested including uranyl chloride, and, when present in sufficient quantities to neutralize the KOH, they, without exception, extinguished the light.

Organic Compounds

Eight organics were added to the luminescing mixture and all failed to produce any change. Many organic compounds such as: Fluorescein, rhodamine B, and sodium naphthionate are, however, known to produce colored chemiluminescence.[2]

Sodium hypochlorite was not placed in the above table although it was included in the tests because I think the results deserve special mention. This compound in very dilute concentrations produced a very good luminescence with only "luminol" and potassium hydroxide. Strong solutions must not be used, however, as they oxidize the luminol much too rapidly, produc-

[2] Plotnikow and Kubal, *Phot. Korr.*, 74, (1938), 97.

ing only a momentary flash. A search of available literature produced no reference to the use of this oxidizing agent in such a reaction and it may not have been observed before. In any event the author's experiments indicate the sodium hypochlorite-luminol-potassium hydroxide mixture to be as good a luminescing mixture as one containing peroxide and sodium ferricyanide. This mixture would, of course, be cheaper than the ferricyanide one and far simpler to make.

In my opinion the importance of the varied concentration experiments is largely overshadowed by the import of the discovery of a new, practicable oxidant for the reaction. Surely the beauty of chemiluminescence need not remain exclusive for the firefly and the chemist's laboratory. Window displays, theaters, etc., all offer possible fields for the commercial applications of chemiluminescence. I intend to investigate more fully the role hypochlorite plays in this reaction.

Reactions in Liquid Ammonia

by Robert Marc Mazo, 17
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➤ In 1896 H. P. Cady was studying qualitative analysis under Edward Curtis Franklin at the University of Kansas. Seeing that Cady was becoming bored with routine classwork, Professor Franklin gave him some extra work in the preparation and analysis of cobalt ammines. In the course of this work, Cady noticed and remarked to Franklin the resemblance between water of crystallization and ammonia of crystallization in the ammines. This was the start of all the work done in this country on the nitrogen system of compounds.

In order to learn something of this field myself, I was faced with the problem of preparing dry liquid ammonia. To liquefy this gas, dry ice was necessary. To prepare the gas I first tried the method taught in school, that of heating calcium hydroxide and an ammonium salt together. It was found, however, that too much heat was needed and not enough gas was produced. The same apparatus was used as in the methods tried later, but results were much poorer. I then tried heating concentrated ammonium hydroxide. More gas was evolved this time but more water was driven off by the heat. The next and final method tried was dropping concentrated ammonia on sodium hydroxide. A satisfactory flow of gas was assured with little moisture and no heat. The final set-up is diagrammed.

After the method of preparing liquid ammonia had been determined, I tried several reactions using it as a solvent. First, I dissolved alkali metals in liquid ammonia. Sodium, potassium and calcium all formed blue-black solutions and crystallized out after the solvent was evaporated, oxidizing very quickly due to the great activity of these metals.

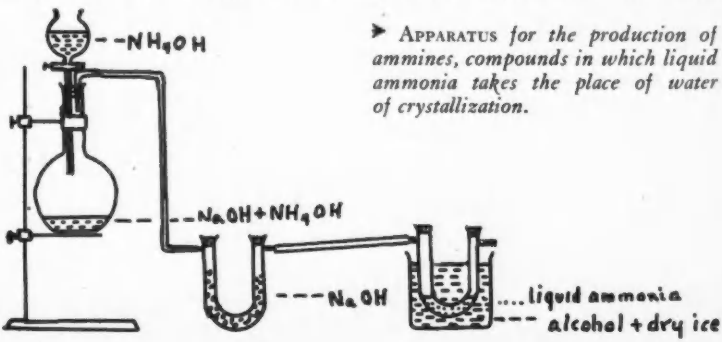
Then I made some ammines, i.e., inorganic salts with ammonia of crystallization. Many beautiful colors were produced by these compounds. I mixed nickel chloride, cobalt chloride and

silver chloride with liquid ammonia. Contrary to the statement of Franklin, the silver chloride did not react. I attribute this to the fact that in its preparation it could not be kept shielded from light. The cobalt chloride ammine gave a pink color and the nickel chloride ammine a blue color. I attempted to determine quantitatively the amount of ammonia reacting with the nickel chloride. I got the result that three molecules of NH_3 combined with every molecule of nickel chloride. I repeated the experiment and calculations and arrived at the same result as previously. In Van Nostrand's Scientific Encyclopedia, the formula for the ammine of nickel was given as $Ni(NH_3)_6Cl_2$. However, it was stated that one or more molecules of H_2O, SO_2, or similar compounds could replace a like amount of NH_3. Therefore, it is reasonable to suppose that in the compound I obtained several molecules of NH_3 were displaced by H_2O, due to the fact that the liquid ammonia was not absolutely dry. Even so, inaccurate balances were probably the reason for the discrepancy. The balance which I had on hand was for photographic use and was supposedly accurate to .1 gram, but in reality was accurate to only about 1 gram. It was the only balance available to me at the time.

While looking in several chemistry textbooks, I found different values for the amount of ammonia in the copper-ammonia complex ion. One book gave the formula for the sulfate salt as $Cu(NH_3)_4SO_4$ and one as $CuSO_4 \cdot 5NH_3$. I did not attempt to determine this value myself. I obtained a value which would correspond to the formula $Cu(NH_3)_8SO_4$.

These ammonia complexes form radicals in which the metal shares electrons with the ammonia to form the complex ion. In the case of the solutions of alkali metals in liquid ammonia, the blue color supposedly is due to the presence of a free electron in the solution, $K \rightarrow K^+ + e$.

In addition to these compounds in which ammonia of crystallization is very similar to water of crystallization, the action of liquid ammonia as an ionizing solvent may readily be likened to that of water. In fact, the nitrogen or ammonia system is analogous to the oxygen or water system in



➤ APPARATUS *for the production of ammines, compounds in which liquid ammonia takes the place of water of crystallization.*

which most chemical reactions are carried out. In the water system, bases are formed from metallic anhydrides and are hydroxides, eg. KOH. The analogous compound of this in the ammonia system is potassium amide, KNH_2.

To prepare this compound, I dissolved potassium in liquid ammonia and added iron filings. The reaction was very slow, taking from twenty minutes to one and one-half hours. Using powdered iron as the catalyst, the reaction was usually complete before one-half hour. The blue color of the metallic solution was replaced by a white solution of the amide. On permitting the excess ammonia to evaporate, the potassium amide turned to potassium hydroxide by taking water vapor from the air so quickly that I was never able to isolate the compound in dry form. However, with a solution of potassium amide I was able to perform reactions analogous to the precipitation of hydroxides by potassium hydroxide. In this manner I prepared zinc amide. I dissolved this compound in an excess of potassium amide solution. The potassium ammonozincate formed was probably similar to the potassium zincate formed by dissolving zinc hydroxide in potassium hydroxide solution.

I also performed several interesting experiments using Diver's liquid as a solvent. Diver's liquid is a compound formed by passing ammonia gas over ammonium nitrate at 0°C. I prepared this with the same apparatus used for the preparation of liquid ammonia, substituting an ice-salt mixture for the alcohol-dry ice mixture. While this compound is not formed from liquid ammonia, it is a member of the ammonia or nitrogen system. The following equation shows the probable formation of the compound:

$$NH_3 + NH_4NO_3 \rightarrow 2NH_3 \cdot HNO_3$$

The ammonia must be closely united with the acidic constituent. It could not exist as a solvent because the boiling point of liquid ammonia as given by Franklin is $^-33$°C. and the liquid is kept at approximately 0°C. It is a strong acid dissolving potassium and zinc rather quickly. When the solution of potassium in Diver's liquid was evaporated, a white solid formed. This was dissolved in water and tested for nitrates. The test showed that it was a mixture of potassium and ammonium nitrates. When the zinc-Diver's liquid compound was tested it gave off brown fumes, NO_2, when sulfuric acid was added. This compound was probably zinc nitrite.

In a great many respects the results I obtained differed from those of Franklin. This, and all my other difficulties, I attribute to the difficulty in preparing absolutely anhydrous liquid ammonia and the large inaccuracies in weighing reagents. At the present time I am trying to devise a way to prepare and keep the liquid ammonia absolutely anhydrous during use. I expect to repeat those experiments requiring measurements using a balance of sufficient accuracy, and anhydrous reagents.

Ethylene glycol is best known as an antifreeze for automobile radiators, but it is used in the processing of textiles and tobacco, and in making low-freezing dynamite, cellophane, synthetic resins and cosmetics.

The Spectrograph

by Alan Johnston, 16.
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➤ In construction of a spectograph at home with a minimum of facilities, the simplest types possess the most appeal. I chose the Barlow type for this reason. It is particularly attractive because it uses the same lens as a collimator and as a camera lens, because the effective dispersion of the prism system is doubled since it is traversed twice by the light, and also because it requires only half the space of the normal type. Two flats are required, which were made of selected pieces of $\frac{1}{4}$-inch plate glass, silvered on the front. Two prisms of the equilateral form with 1-inch faces were provided as a dispersing medium. Even though small, they transmit enough light to give exposures of less than 5 seconds with an arc as a source, and are usually stopped down in use. The lens is one which I have ground and polished; having only one element, as spherical aberation can be corrected with a simple lens, and chromatic aberation causes no image defect in monochromatic light in the spectrograph. The lens has a focal length of 21 inches, giving a dispersion of about 3.20 inches from 4000Å to 8000Å.

In order to secure the spectrum of an element, it must be vaporized. The carbon arc presents the most practical means for accomplishing this, since it is able to give the spectra of at least 70 of the elements. An arc was constructed as a light source for the spectrograph, to operate from the usual house current, 110 v. A.C., drawing from 5 to 7 amperes. The current-carrying carbons are fed by a screw fitting which also serves as the electrical connection. The sample is held either in a small cup in a third carbon or in drilled holes in the current-carrying carbons. The addition of volatile salts to the arc serves to stabilize it greatly and allows the carbons to be drawn further apart, which is an advantage, since it is the light given off by the gases between the carbons which is wanted in the spectrograph.

In the most usual application of the spectrograph, that of qualitative analysis, the bright line spectrum, as emitted by the arc, is used. The value of the spectrograph is due to the fact that the bright lines in the spectrum are fixed in position, and each line is associated with one element. In order to determine which element has produced a line the position of the line in the spectrum must be accurately known.

Since many lines or configurations of lines are easily recognized without knowing their exact position, the relative position of an unknown line can be accurately determined by measurement. Unfortunately, the dispersion of the prism is far from constant, making those measurements only factors in the determination of wavelength. A formula has been developed by Hartmann which will give the wavelength of the unknown line from one measurement if its two constants, which apply only to one setting of the spectrograph and to one reference line, are determined beforehand by meas-

urements taken from three known lines. Although an approximation, the formula fits the curve of prismatic dispersion quite well. The general formula is: $W = W_0 - \frac{bD}{D + a}$

Where W = the wavelength to be determined

W_0 = the wavelength of the reference line

D = the distance from the reference line to the unknown.

a and b are constants.

The constants a and b must be determined from three lines whose positions are known. When the wavelengths and positions of three lines are given the solution of the formula for the constants should proceed as follows.

Let $W - W_0 = y$

y and D will be known, so;

$$y = -\frac{bD}{D + a}$$

$$y(D + a) = -bD$$

$$yD + ya = -bD$$

$$ya = -bD - yD$$

$$b + \frac{ya}{D} = -y \qquad \text{(a)}$$

With data from three lines:

Ca 3933	d = .000
Ca 4226	d = .675
Ca 4455	d = 1.080

Using Ca 4455 as the reference line, two simultaneous equations are set up from:

$y = -229 \qquad d = -.405$

$y = -552 \qquad d = -1.080$

From eq (a) $.565a + b = 229$

$.483a + b = 522$

$.082a = -293$

$a = -3575$

$b = 2249$

Substituted in the original formula, these values for a and b give

$$W = 4455 - \frac{2249D}{D - 3575}$$

When D is expressed in thousandths of an inch.

The formula obtained in this manner gives a very satisfactory fit with other known lines and can be assumed to be accurate with the unknown lines.

Separate from this accurate work on photographs is the field of absorption spectrometry, as applied to light transmitted by liquids and solids. Unlike the flickering arc, the light source is a constant and reliable incandescent lamp, so visual observation becomes simpler and faster than photographic observations. Thru the spectroscope, transparent objects are shown to possess their color because they absorb sections of the spectrum and transmit other sections undiminished. Differences in colors which are similar to the eye are easily detected with the spectroscope. Dyes and indicators are an interesting group for study in this manner. Aqueous solutions of various concentrations can be made up and examined in transmitted light with the spectroscope. The characteristics which give them their colors are easily seen. Absorption of either end of the spectrum is common, and absorption of the middle section may be noticed. However, a solution is seldom found which has absorption bands which are at all narrow. Apart from solutions, the principle of filters is clearly shown, under spectral examination, each type absorbing a certain section of the spectrum in order to give a desired effect on the photograph. One of the experiments conducted in this branch

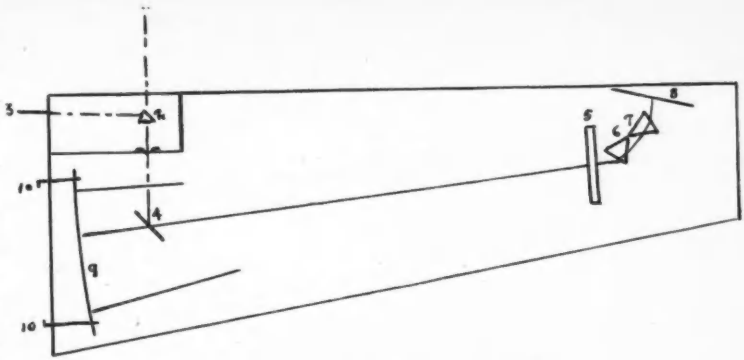

Diagram of the Spectrograph

1. Light source

2. Prism to introduce comparison spectrum without disturbing apparatus

3. Comparison spectrum light source

4. Small diagonal flat

5. Lens

6-7. Prisms

8. Flat to reverse the light beam

9. Film holder

10. Pins to allow film holder to move vertically in order to bring a new strip of film into place, making it possible to record several spectra side by side on one film.

of spectrography was a comparison of basic phenolphthalein and potassium permanganate solutions of equal intensity. While indistinguishable by the eye, they are easily separated with the spectroscope. The permanganate has several narrow bands in the green, while the phenolphthlein had the entire green absorbed. Another along this line deals with the indicators, observing their change in color with the spectroscope as their pH is slowly changed. A solution of methyl orange has a yellow color (basic) caused by the absorption of the violet as seen in the spectroscope. When the indicator changes color from yellow to orange, as the solution is slowly acidified, the spectroscope shows that an additional section of the spectrum, including the blue and green, has been blocked off.

Looking toward the future and the practical aspects of a study of spectrography, of course analysis of specimens excited by the arc is the first and perhaps the most practiced use of the spectrograph. Its speed and accuracy, even in quantitative work, will hold its position here for years to come. However, the science of astronomy would be sorely hindered if not stalled without the services of the utilitarian spectrograph. Distance

means nothing to it; the composition of distant nebulae are as easily found as the value of a "gold" ring. Determination of radial velocities is another important use in astronomy, with more applications than at first appear. I hope, at some time in the near future, to bring together two closely connected hobbies, amateur astronomy and spectrography. I have constructed and mounted a 6-inch reflector and have followed astronomy for several years, and hope to construct a spectrograph for use with the reflector. While not really large enough for serious spectrographic work, the 6-inch telescope would prove an adequate initial companion to a small spectrograph, when provided with an accurate drive in right ascension.

—Photo by Fremont Davis, Science Service Photographer.

➤ A Nobel Prize *winner, Dr. Wendell M. Stanley, discusses problems in medicine and physiology with winners of the Seventh Annual Science Talent Search, during the Science Talent Institute, Feb. 27 - March 2, 1948.*

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